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A SYSTEMATIC STUDY OF THE ACTION OF DEFINITELY RELATED CHEMICAL COMPOUNDS UPON ANIMALS.

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The investigation which we have undertaken has for its object to determine whether it is possible to trace general laws in the action of definitely related compounds upon the animal organization, so that it may be possible to predict, within certain limits at least, what the action of a given substance will be, and what modifications that action will undergo when chemical changes are produced by the replacement of particular elements or groups of elements, or by other definite and generally applicable chemical processes. We hope to be able to offer at least a contribution toward an answer to these questions.

A certain amount of work in this direction has already been done, the results of which we shall cite in their proper places; but as far as we know, nothing approaching a thorough systematic study of the subject has yet been attempted.[1]

[1] See for instances: Brown, A. C., and T. R. Fraser, "On the changes produced by direct chemical addition on the physiological action of certain poisons." Proc. Roy. Soc. Edinb., 1866-9, **6**, 228.

Brown, A. C., and T. R. Fraser, "On the connection between chemical constitution and

The number of questions which arise is of course very great, and the varying conditions both chemical and physiological are very numerous. Even a partial solution of the problem which we have proposed can hardly fail, however, to afford valuable materials for the formation of a system of rational therapeutics.

The plan which we have laid out for our work embraces the following special subjects of study:

1. Related substances belonging to the aromatic series. These offer by far the widest and richest field for study, in consequence of the multiplicity of possible combinations. Thus, to cite a few cases, we have:

a. The comparison of homologous series, as for instance nitro-benzol, the nitro-toluols, etc.

b. The comparison of the properties of ortho, meta and para compounds.

c. The effect of successive replacements of hydrogen by the same molecule, as for example in nitro-phenol, $C_6H_4NO_2OH$, dinitro-phenol $C_6H_3(NO_2)_2OH$, and trinitro-phenol $C_6H_2(NO_2)_3OH$, or again in the case of phenol C_6H_5OH, pyrocatechin o.$C_6H_4(OH)_2$, resorcin m.$C_6H_4(OH)_2$, and hydroquinone p.$C_6H_4(OH)_2$, and finally pyrogallol and phloroglucin $C_6H_3(OH)_3$.

2. Primary alcohols of the series $CRH_2.OH$.

3. Secondary alcohols of the series CR_2HOH.

4. Tertiary alcohols of the series CR_3OH.

5. The amides of the fatty acids beginning with formamide and corresponding anilids.

6. Hydrazines or bodies derived from N_2H_4 by more or less complete replacement of hydrogen.

7. Nitroso-compounds, as for instance nitro-methane.

8. Hyponitrites.

To these we propose to add such others as the progress of our investigation may show to possess special interest. The instances cited will be sufficient to illustrate the general scope and purpose of our work. We have commenced with the study of the relative

physiological action; on the physiological action of the salts of ammonia, of tri-methylamine, and tetramethylammonium" [etc.], *Ibid.* p. 556.

Brown, A. C., and T. R. Fraser, "On the connection between chemical constitution and physiological action, with special reference to the physiological action of the salts of the ammonium bases derived from strychnia, brucia, thebaia, codeia, morphia, and nicotia." Jour. Anat. and Physiol., London, 1868, **2**, pp. 224–242. [Index Catalogue, 1888, **9**, p. 62.]

Also, "Contributions to our knowledge of the connexion between chemical constitution, physiological action and antagonism." By T. Lauder Brunton, M. D., F. R. S., and J. Theodore Cash, M. D. Philosophical Transactions of the Royal Society, Part I, 1884.

action of certain ortho, meta and para compounds, very beautiful preparations of which we owe to the kindness of Prof. Ira Remsen.

To prevent misunderstanding, it may be well to state in this place that Dr. Gibbs is responsible for the plan, general conduct and purely chemical portions of this memoir. The whole of the experimental work has been executed by Dr. Hare. In the discussion of the results of the investigation both will take part. The physiological work was performed in the laboratory of Experimental Therapeutics of the University of Pennsylvania.

Nitrophenols.

Ortho-nitro-phenol.

On the normal dog ortho-nitro-phenol has no apparent effect, as far as the eye can discern, when injected into the jugular vein in the proportion of from 0.002 gram to 0.016 gram to the kilo, nor does this amount affect normal bodily temperature.

Upon the pyrexia produced by cocaine ortho-nitro-phenol evidently acts with some power.

In every one of eight experiments the temperature fell several degrees in from one to two hours, but no marked fall occurred in less than one hour, and we are therefore unable to state positively that the fall of temperature when it did occur was due to the drug or to the fact that the cocaine had largely been eliminated by that time and as a consequence no longer produced fever. This will have to be studied by means of "pepsin fever," which is of longer duration. The doses given to the fevered dogs ranged from 0.002 gram to 0.016 gram per kilo.

On the heart ortho-nitro-phenol has by no means as depressing an influence as its sister, the meta compound; enormous doses rapidly given by the jugular vein being required to produce death, more than 0.1 gram for every kilo. If given by the jugular vein to a dog of 10 kilos in a dose of 0.075 gram the pulse becomes slower, owing to stimulation of the inhibitory apparatus, both peripheral and centric.

Death is produced by cardiac, not respiratory failure, as the animal continues to breathe for some moments after cardiac arrest.

Meta-nitro-phenol.

In three experiments upon dogs this compound exercised no appreciable influence, although the drug was given hypodermically

and the animals were closely watched for as long as six hours and a half. The doses were 0.013 gram to the kilo in one case, in another case 0.044 to the kilo, and in the third 0.072 gram to the kilo.

As regards the effect of meta-nitro-phenol on normal temperature we found that it possesses no power, although the compound was given intravenously, the jugular vein being used. The dose was 0.0033 gram to the kilo.

The influence of the compound on the fevered animal is as yet not positively decided, although we believe that but a few more experiments are necessary to decide this point. In two of the four experiments made by us the thermo-genetic agent was cocaine, and in these meta-nitro-phenol failed to cause a fall. In the remaining two animals in which pepsin was used to produce the fever this compound produced a fall of temperature equal to 2°.1 Fahr. in one case in 50 minutes, while in the second case the fall was 0°.7 Fahr. in 35 minutes. In the two cocainised animals the dose of the drug was 0.005 gram to the kilo and 0.071 gram to the kilo respectively, while in the pepsinised dogs it was 0.0625 gram to the kilo and 0.018 gram to the kilo.

We believe that the explanation of these apparently contradictory effects is very readily reached, not by the variation in dosage, for in the cocainised dog one of the doses was larger than that given to either pepsinised animal, but in the fact that cocaine produces such a violent storm of fever heat as to sweep all things before it unless they are very powerful in their anti-pyretic influence. Thus we have seen 0.062 gram of cocaine given by the jugular vein raise the rectal temperature of a large dog 6° Fahr. in less than an hour.

Further experiments are therefore necessary before we can consider meta-nitro-phenol as an anti-pyretic of reliability.

It should be remembered that all the studies made in this paper on bodily temperature, unless otherwise stated, were made upon animals free to run about.

On the circulatory system we find that when as much as 0.5 gram of the drug is injected rapidly into the jugular vein of a dog of 6 kilos, death occurs immediately from heart failure due to a direct depressant influence on this viscus. If smaller amounts be given the pulse is slowed by as much as 20 beats per minute, this slowing being caused first by centric, then by a peripheral stimu-

lation of the inhibitory nervous apparatus governing the heart. The drug, however, cannot be considered in any way dangerous to the heart when taken by the stomach.

Para-nitro-phenol.

When this drug is given hypodermically to dogs in the proportion of from 0.011 gram to 0.020 gram to the kilo it produces absolutely no effect as far as can be seen.

On the normal temperature, as taken in the rectum, the drug given in the dose of from .0025 to .003 gram to the kilo raises the bodily temperature from 1°.3 Fahr. to 1°.8 Fahr., the animal being free to run about. The influence of this compound upon the temperature of fevered animals we have not yet studied.

When as much as 0.01 gram to the kilo of para-nitro-phenol is injected very rapidly into the jugular vein of a dog, death immediately occurs by cardiac arrest, not of inhibitory origin, for paralysis of these nerves in no way influences the result.

If on the other hand the injection is very slow indeed, so that but small amounts reach the heart at once, only slight and temporary cardiac depression results. After the lapse of ten minutes the pulse becomes very rapid, while the blood pressure, now no longer depressed, rises to the normal or above it. We have proved that this rapidity of circulation is due to a palsy of the peripheral inhibitory nerves of the heart. Half an hour later the pulse becomes slower by ten to twelve beats per minute, and simultaneously there is a fall of arterial pressure, evidently due to an action on the vaso-motor system, since asphyxia at this time produces no rise.

From these results on the higher animals it is evident that the nitro-phenols are possessed of little power over the nervous system, and our studies upon the frog have proved this conclusion to be correct. Indeed, we do not think that we have ever seen any substances which affect the heart so powerfully as do these agents and yet influence the nervous system so imperceptibly.

Ortho-nitro-phenol, the least poisonous of these substances, when given in the dose of .001 gram to the gram of frog seems to exert no perceptible influence on the nervous system, and even the heart is not sufficiently involved to give rise to much general disturbance. When as much as 0.0032 gram to the gram is used, slight evidences of weakness show themselves.

When meta-nitro-phenol is injected into the posterior lymph-sac in the dose of 0.0015 gram to the gram of the frog, no symptoms appear for some minutes. After the lapse of half an hour, however, the animal becomes relaxed and inactive, though the muscles and nerve trunks react well to galvanic stimulus. That there is no impairment of function in the nerves or muscles is proved by the fact that if one limb is protected from the poison, the unprotected nerves and muscles respond equally well to stimulation, and that the spinal cord is unaffected is proved by the fact that reflexes are preserved till death. The heart invariably stops in diastole, the ventricle being full of blood. In one experiment in which the dose was 0.009 gram to the gram of frog, marked dicrotism of the heart was noted.

In our studies of para-nitro-phenol, which it will be remembered was the most lethal of the group in mammalia, we find that when .020 gram of the compound is injected into the posterior lymph-sac of a frog weighing 40 grams, the batrachian immediately becomes relaxed and torpid and in less than five minutes dies from cardiac failure, the heart stopping in diastole with an engorged ventricle. The fatal result is so rapid in its onset and the heart is so evidently affected from the first that we believe the partial lack of response to peripheral irritation which occurs at this time to be solely due to approaching death, since repeated experiment has shown that the nerve trunk and muscles when stimulated with electricity respond perfectly.

Summary.

The lethal doses of the phenols in the dog are as follows:

Ortho-nitro-phenol produces death when only .1 gram is given for each kilo.

Meta-nitro-phenol when given in the dose of a little more than 0.1 gram to each kilo. To every three kilos it will not produce death.

Para-nitro-phenol produces death when as much as 0.01 gram to the kilo is given by the jugular.

The toxicity of these compounds is therefore as follows: para, the most poisonous; meta the next; ortho the least. We shall discuss the subject more fully hereafter.

All the nitro-phenols produce death by paralysing the heart, and not by a respiratory action.

They have very little effect over bodily heat even in fever, the meta compound seeming to be the most powerful in this action. Curiously enough, the ortho and meta compounds stimulate the vagus nerves, while the para compound appears to depress them. On the nervous system their action is probably indirect and is certainly very slight indeed.

It has been noted that every animal killed by the use of the phenols, or after the injection of a less than lethal dose, putrifies rapidly, becoming intensely swollen, while other animals killed by other means and lying in the same vault suffered as yet no change.

Nitranilines.

Ortho-nitraniline.

When 0.5 gram of ortho-nitraniline is administered by the mouth to dogs of from 4 to 10 kilos, no symptoms appear for about ten minutes; after the lapse of which, violent sneezing comes on, the animal sneezing once a minute on the average. Five minutes later these paroxysms become so severe that the head is struck against the floor with each expiratory movement. There is no evidence of nasal irritation, save pawing at the nose at rare intervals, no increase of secretion save the moisture driven out by the drafts of air. The sneezing lasts about forty minutes, then ceases entirely and is followed by no signs of depression. The animal seems as well as ever and remains so indefinitely. Four hours after the dose has been given, a single attack of vomiting with the expulsion of a little watery fluid may occur.

When as much as 0.01 gram to the kilo is injected into the jugular vein of a dog, the blood pressure falls temporarily, but instantly rises again to a point above that occupied before, equalling 16 mm. The pulse rate remains about the same for about seven minutes, then becomes slower by many beats; this is probably due to certain struggling respiratory movements which occur at this time, as it does not occur in the curarised animal. Ten minutes later the pulse rapidly becomes slower, dropping in five minutes from 186 to 90 per minute, and in the course of one minute more to 60. Section of the vagi at this time causes a very slight increase in rate, which, of course, points to stimulation of these nerves peripherally. Here again this apparent action is proven a real one by the fact that if atropine is now given in large

enough dose to paralyse the vagus, the pulse immediately becomes rapid, reaching 174 beats per minute.

The lethal dose of this compound is 0.30 gram to the kilo; 0.15 will not kill when given by the jugular. After death from the drug the blood is found dark and grumous looking, and the spectroscope shows the presence of methaemoglobin.

When 0.043 gram of ortho-nitraniline is injected into the posterior lymph-sac of a frog weighing 32 grams, there is some irritation produced by the acid required to dissolve the compound. Three minutes after the injection the reflexes are found to be intact, but the respirations are noted as having ceased, so far as the movement of the throat and sides is concerned. Following this the reflexes appear to fail quite rapidly and relaxation of a marked type comes on. Irritation of the foot fails to call forth any drawing away of that member, but the tremors of the muscles of the thigh show that the sensory impulse travels upwards at least to some extent. Later, however, sensation is completely lost, for burning of the foot causes no withdrawal, although motion is fairly well preserved. That this loss of sensation is due to an action on the spinal cord, on its sensory side, is proved by the fact that if a ligature is placed around the blood-vessels of a limb and the drug injected below the ligature, this failure of sensation does not occur.

Quite early in the poisoning the heart becomes very much slower than before, finally beating only 24 beats a minute. Its movements at this time are also very feeble; indeed, the circulation at this period is so much impaired that we believe that the symptoms noted are largely due to failure of this part of the organism. Finally, after progressive failure the heart stops in wide diastole.

Meta-nitraniline.

Meta-nitraniline, when injected into the jugular vein of a dog weighing 7 kilos in the dose of 0.5 to 0.8 gram, causes no appreciable fall of pressure, but a very marked slowing of the pulse, amounting to as much as forty beats a minute; slowing which we have proved to be in part due to peripheral "vagal" stimulation, for section of these nerves causes by no means as great an increase of rate as is normal. The slowing cannot be due to an action on the heart, for there is, as already stated, no change in pressure or in pulse force.

When 0.085 gram of meta-nitraniline is given to a frog weighing 25 grams hypodermically, in eight minutes the respirations become somewhat increased in number, and reflex action is also rendered more excitable. This condition lasts for some minutes, and is succeeded by a return to the normal state or one of reduced reflex activity. Five minutes later the reflexes become markedly lessened, and at this time the frog will remain on his back when so placed.

The respirations, which before the dose of the poison were 44, now change to 54. No further change in the reflexes occurs, and it is also to be remarked that the muscles and nerves still respond to electrical stimuli with apparently their normal tone. The spinal cord also responds readily to stimuli. It is evident that the compound has little influence over the nervous system of the frog, except very indirectly. If the substance is given to the dog or rabbit by the mouth, in a short time the animal passes into a condition of quietude and lies down in a state bordering on sleep, if the dose has been as much as 0.10 gram to the kilo or 0.30 gram to the kilo.

In our belief, these symptoms are all due to the influence which the compound exercises on the blood, and spectroscopic examination of this fluid shows the presence of methaemoglobin. This view is also supported by the results reached in the frog, for in these animals there was no direct involvement of the nervous system, but an evident indirect action of the compound. The symptoms produced are also remarkably like those of ordinary aniline poisoning, for there is profuse salivation, total loss of muscle tone, and so great an amount of relaxation that it is difficult to distinguish it from palsy. The reflexes of the eyelids are perfectly preserved, showing that general paralysis is not present.

Para-nitraniline.

The effects of para-nitraniline are much more marked and severe than are those of ortho- or meta-nitraniline. Given to a dog of 4½ kilos in the dose of 0.5 gram, in thirty minutes the springy gait is lost and an unsteadiness in movement is noted, the head is held high in air, and a peculiar guttural note is given forth. Later he staggers as if drunk, the saliva forms from the mouth, and urine is passed of a greenish yellow color. The retching and vomiting upsets the equilibrium of the animal and he falls, and in

an hour passes into apparent unconsciousness, but the eye reflexes are perfectly intact. A curious paroxysm of Cheyne Stopes, breathing and barking, comes on every five minutes by the clock and lasts sixty seconds. Running movements accompany the yelps as the animal lies on its side. Death occurs in coma three hours after the administration of the dose.

When para-nitraniline is injected into the jugular vein of a dog, in the dose of 0.003 gram to the kilo, in the space of 70 seconds it produces a slight fall of arterial pressure and pulse rate, the slowing of the latter becoming more and more marked until the decrease from the original rate equals 50 beats a minute. That the fall of blood pressure is rather the result of momentary disturbance caused by the injection than any special action, is proved by the fact that asphyxia instantly causes a rise. These same changes occurred in another instance where the dose was 0.002 to the kilo.

That the slowing of the pulse is due to a stimulation of the peripheral vagi is proved by the fact that section of these nerves causes almost no increase in pulse rate, and also because at this time the tracing showed no evidence of cardiac depression.

In experiment No. 3, where but 0.0007 gram was given to each kilo, no change of any moment occurred save that when the vagi were cut the pulse failed to increase its rate as it should do in the normal animal. In experiment No. 4 0.033 gram to each kilo was injected in divided doses, but no other changes than those already noted.

That the slowing of the pulse is due to peripheral vagal stimulation is proved by the fact that atropine injected into the circulation prevents this change in the pulse when para-nitraniline is given. The fatal dose of this compound when injected into the jugular is .040 gram to the kilo.

Summary.

The lethal dose of ortho-nitraniline is about 0.3 gram to the kilo of animal. It slows the pulse by stimulating the peripheral vagi and produces methaemoglobin in the blood. The action on the nervous system consists chiefly in an effect on the sensory side of the cord, but probably depends on the changes in the blood, and is slight and indirect. In large amount the drug is a powerful cardiac depressant.

The sneezing produced by it when given by the stomach is the most curious symptom produced.

Meta-nitraniline also stimulates the peripheral vagi, thereby slowing the pulse. The nervous effects are very feeble and depend upon the changes in the blood, namely, the development of methaemoglobin, all the symptoms being those of aniline poisoning.

Para-nitraniline is by far the most poisonous member of the group, and acts like the other members in a stimulating manner on the peripheral vagi.

The lethal dose of it is 0.04 gram to the kilo by the jugular vein.

Amido-benzoic Acids.

The Amido-benzoic Acid Group.

With a few exceptions it may be stated that this class of substances are without any effect upon the animal organism. Whether they are given to animals by the stomach or intravenously, the normal condition of the system remains unchanged in its functional activity.

Ortho-amido-benzoic Acid.

The administration of 2 grams of this substance for every 8 kilos of dog's weight was entirely without effect.

Profuse urination occurred in one instance, given below, six minutes after the ingestion of the dose, and could not therefore have been due to the action of the drug.

Dog weight, 8 kilos; 3.25, rectal temperature 103.2.

3.32, 2 grams of drug by oesophageal tube in 40 cc. aq.

3.38, has urinated profusely.

3.40, has defecated loosely.

4.25, no other symptoms; rectal temperature 103.

The next day the animal was perfectly well.

On the circulation the results are almost equally barren. After the injection of 1 gram for every 6 kilos by the jugular vein, no symptoms appear for about 9 minutes, when a decided slowing of the pulse occurs. As this occurs both in curarised and non-curarised animals, it must depend on some direct effect of the drug. Further experimentation has shown that the inhibitory nerves are stimulated centrically and peripherally, since under these circumstances section of these nerves causes slight increase in rate not

equal to that occurring in the normal dog, a fact which points to peripheral inhibitory stimulation. This peripheral action would seem proved, since atropine failed to produce an increase in rate when ortho-amido-benzoic acid was given first.

Meta-amido-benzoic Acid.

This compound also has no influence over the animal economy, as will be seen in the following examples of some of the experiments in which no change in bodily temperature or general condition occurred:

Dog weight, 4 kilos; 12.26, rectal temperature 103.
12.28, 1 gram of compound in 40 cc. aq.
12.31, vomited 10 cc. of dose.
1.40, no symptoms; rectal temperature 102.8.
2.30, no symptoms; rectal temperature .

Dog weight, 5 kilos: 12.30, rectal temperature 99.5.
12.22, 2 grams of compound in 40 cc. aq.
12.50, vomited about 10 cc.
1.40, no symptoms; rectal temperature 100.
2.30, no symptoms.

Careful manometrical studies of the circulatory apparatus after doses of the compound by the jugular vein give results identical with those already given, and even so much as 1 gram to every 5 kilos of the dog's weight produces no influence. In one experiment in which the entire mass of the injection (1 gram in 40 cc. aq.) was sent *en masse* into the heart, there was for a moment a fall of blood pressure of about 20 millimeters of mercury, which lasted for only 10 seconds, and was dependent on the rapidity of the injection.

When para-amido-benzoic acid is given by the stomach to a dog, so that for each 7 kilos of the animal 500 milligrams of the drug are used, nothing occurs, and this is likewise true when such a large dose as 2 grams to every 5 kilos are employed; in one case slight vomiting came on, but as a very small amount of liquid was ejected, none of the drug was lost, and it is probable that the efforts at vomiting were largely volitional and due to the irritation of the fauces by the oesophageal tube used when giving the dose. No fall in the normal bodily temperature occurred, as was proved by the insertion of a rectal thermometer before and after dosage.

Urination came on one hour after the dose was given, but the quantity passed was small in amount and probably had no dependence on the drug. The two following experiments give results similar to those found in all the others:

Dog weight, 7 kilos; 11.30, rectal temperature 102.1.

11.35, 500 milligrams of drug by oesophageal tube in 60 cc. of water.

1.05, no symptoms whatever so far.

2.05, no symptoms whatever so far.

Next day, no symptoms as yet.

Dog weight, 5 kilos; 12, rectal temperature 102.5.

12.02, 2 grams of drug as before.

12.15, vomited about 5 cc. of liquid, but no drug.

12.35, rectal temperature 102.5.

1.40, rectal temperature 102.5; no symptoms whatever so far.

1.45, urinating slightly, about 60 cc.

On the circulation, as studied by the mercurial manometer, this compound gives results of no more importance than those already stated. The pulse rate and arterial pressure undergo no changes when doses of from 500 milligrams to 1 gram to every 8 kilos of the dog's weight are given by the jugular vein in the space of 10 seconds in 30 cc. of sodium carbonate solution.

Nitro-benzoic Acids.

Ortho-nitro-benzoic acid when injected into the jugular vein of the dog, or when given by the stomach, in the dose of 1 gram to every 4 or 5 kilos, seems to have very little, if any, influence over the animal free to run about, only a very slight relaxation of the general system being evidenced by a desire to keep quiet. That this tendency to be quiet and still is rather the result of the operation of opening the jugular vein, or forcing the drug into the stomach, is proved by the fact that the animal walks without difficulty and responds to caresses.

It is to be noted, too, that the symptoms of depression, such as they are, are in part due to the use of a saturated solution of sodic carbonate as a solvent of the drug. That such a solvent is in no way injurious to the compound itself is well known, as the salts of the blood change all such acids into sodic salts as soon as they enter the circulation. The bodily temperature remains unaffected.

If ortho-nitro-benzoic acid is injected by the jugular vein in the same dose as just mentioned (1 gram to every 4 or 5 kilos), there are no changes of note in the arterial pressure or pulse rate, even though the solution is concentrated and rapidly injected.

Given to the frog hypodermically it seems equally innocuous, and we therefore have reached the conclusion that this compound is a substance possessing almost no influence over the body in ordinary amounts.

Meta-nitro-benzoic Acid.—If this compound is injected into the jugular vein or stomach of an animal free to move about, in the dose of from 0.25 gram to 1 gram to every 7 kilos, no more symptoms ensue than follow the use of the preceding salt.

Correspondingly we find that the circulatory apparatus remains unaffected, and that both the pulse rate and arterial pressure are undisturbed, and it is therefore almost inert physiologically in the doses named.

Para-nitro-benzoic Acid has also an equally feeble influence, and the entire group seems to be alike in its harmlessness.

(*To be continued.*)

ON PENTAMIDOBENZOL.[1]

By A. W. Palmer and C. Loring Jackson.

Nearly two years ago, in a paper upon Tribromtrinitrobenzol,[2] one of us in conjunction with J. F. Wing described some attempts to reduce triamidotrinitrobenzol, and announced that the work would be continued. Before doing this, however, it seemed advisable to try similar experiments with the triamidodinitrobenzol, as this substance can be obtained much more easily, and the experience gained in this way would be useful when we returned to the much less accessible trinitro compound. Accordingly, we have undertaken together the work on the dinitro compound, which has led, as we had hoped, to the preparation of the

[1] From the Proceedings of the American Academy of Arts and Sciences, communicated by the authors.

[2] This Journal **10**, 283 (1888).

chloride of pentamidobenzol; but, shortly after we had sent to the *Berichte der deutschen chemischen Gesellschaft* a preliminary notice[1] of this substance, a number of the same journal reached us containing a paper by Andrew Barr[2] in which the chloride of pentamidobenzol was also described, and, as this paper, although it came into our hands after our preliminary notice had been sent, was presented to the German Chemical Society a fortnight before ours was written, we have dropped this line of work in order to avoid interfering with Barr, or Merz, in whose laboratory the research of Barr was carried on, and publish in this paper the results which had been already obtained by us when we received Barr's paper. The method of making pentamidobenzol used by us is different from that of Barr, who prepared the diamidotrinitrobenzol from the ethylether of trinitroresorcine and alcoholic ammonia, and then reduced this product with tin and hydrochloric acid, whereas we submitted to a similar reduction the triamidodinitrobenzol made by the action of alcoholic ammonia on tribromdinitrobenzol. Both this triamido and the corresponding trianilido compound are new, and an account of them is therefore included in this paper.

Triamidodinitrobenzol, $C_6H(NH_2)_3(NO_2)_2$.

This substance was prepared by treating tribromdinitrobenzol,[3] melting point 192°, with alcoholic ammonia; but this action takes place much less easily than in the case of the corresponding trinitro compound, for whereas that was attacked by alcoholic ammonia in the cold, and the reaction was rendered complete by short boiling in a flask with a return condenser, the dinitro compound gave no action with alcoholic ammonia in open vessels, but it was necessary to heat the two substances under pressure in the water-bath to bring about the reaction.

As we had no digester fit for this purpose, we were obliged to heat the mixture in soda-water bottles, which were kept in a boiling water-bath for about eight hours. The contents of the bottles at the end of this time consisted principally of a mixture

[1] Ber. d. chem. Gesell. **21**, 1706 (1888). [2] Ib. **21**, 1542 (1888).

[3] The tribrombenzol used in making this substance must be purified by crystallisation from alcohol after it has been distilled, as, if this crystallisation is omitted, a substance melting in the neighborhood of 95° remains mixed with the tribrombenzol, and gives rise to very impure products after the treatment with nitric acid. The nature of this impurity will be considered in another paper.

of dark reddish yellow needles with nearly black amorphous masses. There was also a colored alcoholic solution, which on evaporation left a red amorphous substance with a comparatively low melting point; but this was formed in such small quantities that we did not attempt to study it beyond ascertaining the fact that it is not altered by further heating with alcoholic ammonia. The tribromtrinitrobenzol, when treated with alcoholic ammonia, forms a similar by-product,[1] soluble in alcohol, which is now under investigation. The two products of the reaction which were not dissolved in the alcohol were separated mechanically, washed thoroughly with various solvents, and analysed without further purification, as they both showed such a slight solubility in all the common solvents that a crystallisation of them in any quantity was a matter of very great difficulty. In spite of the great difference in their appearance they both had the same composition, that of the expected triamidodinitrobenzol, as is shown by the following analytical data, in which Analyses I and II were made with the reddish yellow needles, Analysis III with the black amorphous body.

I. 0.3000 gram of the substance crystallised in yellow needles gave on combustion 0.3710 gram of carbonic dioxide and 0.1085 gram of water.

II. 0.1510 gram of the crystalline substance like that used in I gave 42.4 cc. of nitrogen at a temperature of 8.6° and a pressure of 748.5 mm.

III. 0.3028 gram of the substance deposited in black amorphous masses gave on combustion 0.3778 gram of carbonic dioxide and 0.0925 gram of water.

	Calculated for $C_6H(NH_2)_2(NO_2)_2$.	Found. I.	II.	III.
Carbon	33.80	33.73	...	34.02
Hydrogen	3.28	4.02	...	3.39
Nitrogen	32.87	...	33.31	...

Properties.—The triamidodinitrobenzol, as deposited by the action of alcoholic ammonia on tribromdinitrobenzol, forms either reddish yellow needles, or nearly black amorphous masses. When the substance is crystallised from a mixture of chloroform and alcohol, which can be done only with great difficulty on account of its slight solubility, it forms microscopic yellow plates, or broad

[1] This Journal **10**, 290.

flattened prisms, and, if the treatment with the mixed solvents is carried on in a continuous extracter, these crystals collect into characteristic yellow masses shaped like an S or U. It does not melt even above 300°, but is decomposed if heated more intensely. It is very slightly soluble in alcohol or chloroform, although it imparts a perceptible yellow color to these solvents; more soluble in nitrobenzol, but cannot be obtained in crystals easily from this solution, so that a mixture of alcohol and chloroform is the best solvent for it. In the other common solvents it is either entirely insoluble or very slightly soluble. In this respect it resembles the corresponding trinitro compound, but it is, if there is any difference, slightly more soluble than that. The substance does not form definite salts, although it dissolves easily in concentrated hydrochloric acid, forming a dark red liquid. It shows therefore a greater tendency to form salts than the triamidotrinitrobenzol, which is insoluble in strong hydrochloric acid.

Trichloride of Pentamidobenzol, $C_6H(NH_2)_3(NH_3Cl)_3$.

To prepare this substance, some of the triamidodinitrobenzol (either the crystalline or amorphous) was heated on the water-bath in a flask with strong hydrochloric acid, a very strong solution of stannous chloride, granulated tin, and some pieces of platinum foil. After some hours the very deep red solution had lost most of its color, but still showed a dirty brownish yellow tint; it was then allowed to cool, when crystals were deposited, which increased in quantity, if the liquid was saturated with hydrochloric acid gas. The crystals were filtered out, and washed with concentrated hydrochloric acid, then, as we did not succeed in removing the salts of tin completely by precipitation from an aqueous solution with hydrochloric acid gas,[1] the substance was dissolved in very little water and the solution saturated with sulphuretted hydrogen, the stannic sulphide formed was filtered out, and the filtrate, after freeing it from sulphuretted hydrogen with a stream of air, once more saturated with hydrochloric acid gas, which threw down the substance in an essentially pure state and nearly white. In all this work care must be taken to avoid heating the solutions, as the chloride of pentamidobenzol, after the reducing agents have been removed, is easily decomposed by heat into a black tar; the solutions, therefore, should never be

[1] Barr succeeded in removing all the tin from his preparation in this way.

concentrated by evaporation on the water-bath. We obtained a less pure substance also, if the solution in water and precipitation with hydrochloric acid gas was repeated more than once. The crystals were dried at first in a desiccator over calcic oxide, calcic chloride, and potassic hydrate, and finally heated to 70°–80° for about five hours in an air-bath. On analysis they gave the following results:

I. 0.2372 gram of the substance gave on combustion 0.2445 gram of carbonic dioxide and 0.1157 gram of water.

II. 0.1827 gram of the substance gave 0.1880 gram of carbonic dioxide and 0.0880 gram of water.

III. 0.1533 gram of the substance gave 35.8 cc. of nitrogen at a temperature of 14.2° and a pressure of 750 mm.

IV. 0.1457 gram of the substance gave according to the method of Carius 0.2377 gram of argentic chloride.

	Calculated for $C_6H(NH_2)_3(NH_3Cl)_2$.	Found. I.	II.	III.	IV.
Carbon	27.43	28.11	28.06	...	...
Hydrogen	5.33	5.42	5.35	...	...
Nitrogen	26.67	...	...	27.08	...
Chlorine	40.58	...	...	...	40.33

Considering the ease with which the substance is decomposed, the agreement between these results and those calculated from the formula is as close as can be expected. The method of purification described above, however, does not always give such satisfactory results. Samples from two other preparations gave numbers which differed by about one per cent. from those corresponding to the formula, the chlorine being too low and the other constituents too high by this amount; but we ascribe this to partial decomposition of the substance during the purification, as both of these specimens were much darker in color than that which gave the more satisfactory analyses. The objection which might be founded on these results, that our substance was not a definite compound, but a mixture of ammonic chloride with some organic body less rich in nitrogen than the chloride of pentamidobenzol, is removed by the microscopic examination of the substance, which showed that it consisted of well-developed rhombic crystals without any admixture whatever, to which may be added the fact that chlorplatinic acid gave no precipitate with a solution of the substance.

Properties.—The trichloride of pentamidobenzol, as precipitated by hydrochloric acid from its aqueous solution, is seen under the microscope to consist of rather thick well-developed transparent rhombic plates, with the sharper angles truncated by a single plane. It is colorless when first prepared, but soon turns pink or gray, and on long standing passes through dark brown to black, a change which is much accelerated by heat; yet even after it has become nearly black, if examined with the microscope, it is found to retain unaltered its crystalline form, and the individual crystals are still transparent, although very much darkened, so that this change in color seems to have taken place only superficially. It is very easily soluble in water, but only slightly soluble in strong hydrochloric acid, a property which is useful in the purification of the substance. The aqueous solution decomposes quickly when heated, a black tar being formed, and a similar change takes place more slowly at ordinary temperatures, the solution becoming at first clear pink, and then darkening through shades of red to black. The action of more violent oxidising agents is described below, and resembles that of the air. The salt, when dry or moistened with strong hydrochloric acid, is much more stable than a solution, or the wet salt. The substance is sparingly soluble in alcohol and essentially insoluble in ether, benzol, or chloroform.

If ammonic hydrate is added with caution to a concentrated solution of the salt, a black jelly is precipitated; if the solution is dilute, no precipitate is formed, but the liquid takes on a pink color, which in a few minutes passes through purple and violet blue to a yellowish green; from this solution hydrochloric acid precipitates black flocks, which redissolve in an excess of the acid, or on the addition of ammonic hydrate. Sodic hydrate acts on the chloride in the same way. The free base seems to be insoluble in ether; at any rate, nothing was extracted by this solvent from an aqueous solution of the salt, to which an excess of sodic hydrate had been added. It is evident from the observations just described, that the isolation of the free base would be a matter of great difficulty.

The foregoing results correspond to those of Barr in every respect, except the crystalline form of the chloride, which he describes as white needles as fine as hairs. He also made the pentacetyl compound $C_6H(NHC_2H_3O)_5$.

Chlorplatinic acid with a solution of the trichloride of pentamido-

benzol gives no precipitate at first, but after some time a slimy brown substance is deposited on the sides of the test-tube, evidently a product of oxidation. We are inclined to think, however, that the oxidising agent is the oxygen of the air rather than the chlorplatinic acid, as a similar result was obtained by the action of picric acid. Benzaldehyd added to a solution of the salt also gave a tarry product.

When the trichloride of pentamidobenzol is treated with nitric acid and ferric chloride, a deep purple solution[1] is formed, looking very much like potassic permanganate; and when an excess of the ferric chloride has been added, a brown flocculent precipitate is deposited, which when dried forms a hard mass of a brown color without crystalline form, since under the microscope it appears to be made up of sandy granules. It is slightly soluble in water, imparting to it a dark brown color. Preliminary analyses gave the following results:

0.1600 gram of the substance on combustion gave 0.2592 gram of carbonic dioxide and 0.0650 gram of water.

0.1685 gram of the substance gave according to the method of Carius 0.0797 gram of argentic chloride.

	Found.
Carbon	44.18
Hydrogen	4.51
Chlorine	11.69

We were engaged on the study of this substance when we received Barr's paper, and accordingly stopped our work on this subject, and we publish these analyses only because they may be of use to any one who may continue the investigation of this substance, as it would be idle to try to derive a formula from them until they have been supported by further work. Barr also observed the formation of this substance, but did not attempt to study it carefully, or analyse it.

It seems probable that the pentamidobenzol, in addition to the trichloride, can form a *pentachloride*, as one of our first preparations, in which the reduction was carried on at a lower temperature than usual, yielded a substance which, dried at first in a desiccator over calcic chloride without any alkaline absorbent, and finally for a short time in an air-bath at 90°, gave the following result on analysis:

[1] Compare this with the action of air on a solution of the salt or of the free base described earlier in this paper.

0.1738 gram of the substance gave 30.9 cc. of nitrogen at a temperature of 6° and a pressure of 750 mm.

	Calculated for $C_6H(NH_2Cl)_3$.	Found.
Nitrogen	20.86	21.37

The appearance of Barr's paper has prevented us from making another attempt to prepare this substance. If it is a definite compound, it is a very unstable one, as it gave off a distinct smell of hydrochloric acid.

Trianilidodinitrobenzol, $C_6H(C_6H_5NH)_3(NO_2)_2$.

This substance can be made by heating for a short time aniline with tribromdinitrobenzol in the proportion of six molecules of the base to one of the bromine compound. It seems that the two substances do not act on each other in the cold, or, if there is any action, it is a very slow one, and in this respect the dinitro compound differs from the tribromtrinitrobenzol, which acts on aniline quickly at ordinary temperatures. The product was purified by crystallising it from alcohol till it showed the melting point 179°, dried at 100°, and analysed with the following results:

I. 0.1820 gram of the substance gave on combustion 0.4347 gram of carbonic dioxide and 0.0760 gram of water.

II. 0.1906 gram of the substance gave 26 cc. of nitrogen at a temperature of 12° and a pressure of 762 mm.

III. 0.1815 gram of the substance gave 26 cc. of nitrogen at a temperature of 17° and a pressure of 743 mm.

	Calculated for $C_6H(NHC_6H_5)_3(NO_2)_2$.	Found. I.	II.	III.
Carbon	65.31	65.13	...	...
Hydrogen	4.30	4.64	...	...
Nitrogen	15.88	...	16.24	16.24

Properties.—The trianilidodinitrobenzol, when crystallised from alcohol, forms vivid orange-red needles, which under the microscope appear as long prisms terminated by a single plane at angles not very far from right angles to the sides; occasionally groups of radiating needles are observed also. When crystallised from ether, it forms irregularly spherical crowded groups of short stout radiating prisms with blunt ends made up of several planes, a form which is decidedly characteristic. It melts at 179°, and is essentially insoluble in either cold or boiling water, or in ligroine;

slightly soluble in cold alcohol, freely in hot; moderately soluble in ether, carbonic disulphide, glacial acetic acid, or acetone; freely soluble in benzol or chloroform, but the substance is deposited from the two solvents last mentioned in an amorphous form, so that hot alcohol is the best solvent for it. Strong hydrochloric acid, either hot or cold, has no perceptible action on it. Strong nitric acid dissolves a very little, with a pale yellow color; strong sulphuric acid dissolves rather more of the substance, with a stronger yellow color. Upon heating it with either of these last two acids it is charred. It is therefore, as was to be expected, less basic in its properties than the triamidodinitrobenzol.

THE INDIAN GRASS OILS.

[*Preliminary Notice.*]

By Frank D. Dodge.

There are found in commerce at least five volatile oils, which appear to be obtained from various tropical grasses of the genus *Andropogon*. These are: oils of citronella, lemon-grass, Indian or Turkish geranium, ginger-grass, and vetivert or cus-cus. Much uncertainty has arisen in the effort to assign to each oil its proper botanical source, and in the identification of nearly related plants which afford commercially distinct oils.

The citronella plant appears to be the one known to botanists as *Andropogon nardus*, Linn., and is figured and fully described in Bentley and Trimen's "Medicinal Plants." This grass is quite common in the plains of the Punjab and the North-west Provinces, and is extensively cultivated in Ceylon, Singapore, and the Malabar coast. Some interesting details of the occurrence, uses, etc., of the grass and the manufacture of the oil are given in Watt's "Dictionary of the Economic Products of India" (1888).

As to the origin of "lemon-grass oil" there appears to be considerable doubt. The majority of botanical writers ascribe it to *A. schoenanthus*, Linn., while the best Indian authorities state

that it is obtained from a different plant, which more closely resembles *A. nardus.* Hackel, in his Monograph of the Andropogoneae (1889), leaves the question undecided. The oil of lemon-grass is certainly distinct from all the others, and it seems probable that the grass is a peculiar species.

The important Turkish geranium oil, which also passes under the names of Rusa oil, Palmarosa oil, Nimar oil, and others, is probably derived from *A. schoenanthus,* Linn. It has been known and used for a long period. According to Pickering, the grass was employed as a perfume in the time of Alexander the Great. A description of the plant is given by Dr. Dymock ("Materia Medica of India"), and it is figured as *A. pachnodes* by Trinius (Sp. Gram. III, tab. 237). The grass is abundant in Central and Northern India; the preparation of the oil is described by Dymock, Watt, and others.

Ginger-grass oil appears to be a cheap and inferior variety of the geranium oil.

Oil of vetivert, or cus-cus, is obtained from the rhizome and root-fibres of *A. squarrosus,* Linn. (*A. muricatus,* Retz.). This grass was also known at an early date. It is very probably the sweet-scented "usira" root of the "birana" grass mentioned in the Dhammapada and other Sanskrit classics (Pickering). Vetivert grass occurs in many parts of India, and appears to be cultivated in Burmah. It is also found in Mauritius and the Philippine Islands, and is the only species of those under discussion which occurs in the New World, being abundant in the Antilles, Porto Rico, Jamaica, Brazil, etc. The oil of vetivert is manufactured in this country from grass imported from India, and finds an important application in perfumery.

Examination of Citronella Oil.

Gladstone in 1872,[1] by repeated distillation, separated the oil into two portions, one boiling at 202°–205°, the other at 199°–202°. On combustion, these gave figures from which he calculated the composition $C_{10}H_{16}O$. It is to be noted, however, that his results approximate more closely to the formula $C_{10}H_{18}O$.

In 1875, C. R. A. Wright[2] found the main constituent to be an unstable body of the composition $C_{10}H_{18}O$, which on treatment with dehydrating agents gave rise to a terpene or terpenes, but

[1] Jour. Chem. Soc. (2) **10**, 7.

[2] Jour. Chem. Soc. 1875, 1.

not cymene. The latter was obtained, however, by heating with bromine. He found that the oil was altered by repeated distillation, high-boiling resinous products being formed.

Flückiger, in his "Pharmacographia," made the important observation that both citronella and lemon-grass oils yield solid compounds when shaken up with bisulphite solution. This fact immediately suggested the method of investigation. It appears that Mr. Kremers also (of whose work the writer was unaware until after the results described below had been obtained) took advantage of this observation.

Kremers[1] treated the oil with strong bisulphite solution, filtered out the white precipitate, and washed with alcohol. The bisulphite compound was decomposed by dilute sulphuric acid at a gentle heat, and the sulphur dioxide removed by dry potassium carbonate. The aldehyde obtained thus was a viscid yellow liquid, possessing a geranium-like odor. Its specific gravity was 0.942. On fractionation it decomposed. Analyses gave figures approximating to the formula $C_7H_{14}O$, but the boiling point was not ascertained. From these data the aldehyde was concluded to be a heptoic aldehyde, isomeric if not identical with oenanthol. The oil filtered from the bisulphite compound was by fractionation separated into two portions: one, boiling below 200°, appeared to be an impure terpene, $C_{10}H_{16}$; the other, boiling between 217° and 222°, on analysis gave:

		Calculated $C_{10}H_{18}O$.
C	77.96	77.92
H	12.27	11.69

Kremers found this substance to be different from eucalyptol, and suggested that the name citronellol be retained for it. It is evident that Kremers' results differ greatly from those of Wright. The former is of the opinion that the oil examined by Wright was really a variety of geranium oil, *i. e.* true oil of *A. schoenanthus*, as stated by Wright. According to Watt, however, Dr. Wright's material was probably citronella, erroneously ascribed to *A. schoenanthus.*

Three samples of citronella oil have been examined by the writer. The first is an oil manufactured on the Winter Estate, near Galle, Ceylon. This commands a higher price than other

[1] Proc. Amer. Pharm. Assn, 1887.

varieties, and is considered the purest. The second is what is known as "native" oil, a cheap variety, whose quality is considered uncertain. The third is a "native" oil redistilled in this country.

It is well known in the trade that citronella oils are largely adulterated with kerosene. Large quantities of the latter are imported at Ceylon, and it is quite improbable that all is used for illumination. Detection of the adulteration, however, is not difficult. Samples two and three were found to contain about 18 per cent. of kerosene, while a careful examination of sample one convinced the writer of its freedom from such impurity. All subsequent work was accordingly done on sample one.

This oil is clear light greenish yellow, with a sharp burning taste and rather powerful aromatic odor. Its density at 16° is 0.8770; at 26.5°, 0.8750. This agrees fairly well with Gladstone's figures, 0.8741 and 0.8750 at 20°. Kremers, however, found the density of his material to be 0.8833. On distillation the oil passes over between 200° and 240°, leaving about 10 per cent. of thick oily residue, possessing a pungent odor. Continued fractioning did not yield good results, as the oil appeared to decompose on long heating.

When shaken with a saturated solution of sodium bisulphite, after ten minutes the liquid solidifies with considerable evolution of heat. On standing, the mass becomes yellow on the surface, owing to oxidation of other constituents of the oil. The bisulphite compound is readily obtained pure by thinning with ether or chloroform, filtering, and washing with the same solvents, in which the precipitate is practically insoluble. Alcohol does not work so well. The bisulphite precipitate is readily decomposed by acids, alkalies, sodium carbonate, or hot water, which regenerate the aldehyde. All fractions of the oil yield precipitates with bisulphite solution; the first fractions, however, the more readily.

Phenylhydrazine combines with the oil with evolution of heat. On testing the successive fractions, it was noticed that the first reacted more readily than the others, indicating that the aldehyde or aldehydes were among the more volatile constituents of the oil.

Ammoniacal silver solution, when mixed with the oil and allowed to stand, yields very readily a mirror, followed by a thick lustrous deposit of metal.

Acetyl and benzoyl chlorides react with great readiness, but no

solid compounds could be detected among the products of the reaction. Ammonia under ordinary conditions appears to be without action on the oil.

Isolation of the Aldehyde.

The washed bisulphite compound, freed from ether by short exposure to the air, was gradually added to a warm solution of sodic carbonate and kept warm until all the white precipitate had disappeared. The supernatant oil was then separated and dried. On distillation, the greater part boiled from 200°–210°, leaving a thick residue, which did not react very readily with phenylhydrazine. This indicated an alteration of the aldehyde, due to the heat of distillation. To avoid this difficulty, the oil liberated from the bisulphite compound was immediately distilled in a current of steam. This plan succeeded admirably, a pure white oil passing over, and a small quantity of dark-colored oil remaining in the flask.

In order to ascertain whether possibly a mixture of aldehydes or ketones were present in the oil, a large amount was treated after the following plan:

Pure oil (distilled with steam)

First ½ distillate — Next ¼ — Residual ¼

(Bisulphite separation) — (Bisulphite separation)

(*A*) Aldehyde (*B*) Residual oil (*C*) Aldehyde (*D*) Residual oil.

Should the portions (*A*) and (*C*) differ, it would be fair to assume that there were two or more constituents having ketonic properties. If they were found to be identical, probably but one aldehyde was present in the oil.

2 liters of oil were treated in this way. For the preparation of the aldehyde, the first portion of the distillate (1100 cc.) was divided into four parts of about 280 cc. each. The bisulphite solution contained 1000 grams dry sodium bisulphite dissolved in 2 liters of water. 250 cc. of this was added to each portion of oil and the mixture well stirred. During the stirring the vessels were kept cool with ice water. After about ten minutes the mixture "set," forming a snow-white magma. The remainder of the bisulphite was now added gradually, stirring all the time. A further evolution of heat took place until all the oil had been precip-

itated. After standing about an hour the mass was wrapped in flannel, and after draining on a large funnel, was carefully pressed in a filter-press. When the mass was pretty dry it was removed from the press, thinned out thoroughly with ether, and again drained and pressed. The bisulphite compound was now tolerably free from residual oil. To remove the ether it was exposed to the air for several hours. At this stage it has the appearance of wax or soap; on long exposure it decomposes, turning yellow on the surface.

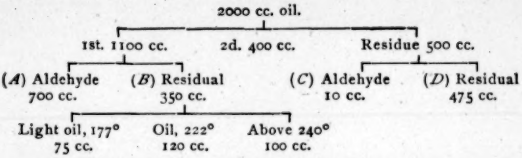
To liberate the aldehyde, the dry mass was mixed with crystallised sodic carbonate, 450 grams of the former to 350 grams of the latter, in a large flask. Steam was then passed into the mixture, which soon liquefied and yielded a distillate of, in this case, about 250 grams. The total yield of aldehyde (portion *A*) amounted to 700 cc.

The filtrate from the bisulphite precipitate was then worked up. The oil yielded by the first pressing was collected apart. The ethereal washings were dried and, after removal of the ether, combined with the first. The product, a light yellow oil of peculiar odor, amounted to about 350 cc.

This oil was now carefully fractionated. It commenced to boil at 185°, and the temperature rose steadily to 240°, above which it was considered unnecessary to fraction. At the tenth distillation the oil was almost completely separated into three portions. The first, a limpid colorless oil having a lemon-like odor, boiled at 177°–180°, and amounted to 75 cc. The second, a somewhat thicker oil, of slightly greenish color and having a pleasant rose-like odor, boiled at 222°–224°, and amounted to 120 cc. The third portion consisted of products boiling above 240°, and was a dark-brown viscid liquid having a pungent odor.

The residual 500 cc. of oil, not readily volatile with steam, was treated with bisulphite in the same manner as the first portion, but using much less bisulphite. After a few days the bulky precipitate was filtered out, pressed, washed, and the aldehyde liberated as before. About 10 cc. only were obtained, which resembled in appearance, odor, taste, and behavior on heating, the aldehyde obtained from the first distillate, and is almost certainly identical with it.

The results of the analysis may be concisely represented by the diagram:



The second distillate of 400 cc. was not further examined. The portion (*D*) was fractionated. It behaved like portion (*B*), but yielded a much larger amount of high-boiling products, which oxidise readily and are difficult to treat.

Properties of the Aldehyde.

The steam-distilled aldehyde, after drying several days over calcic chloride, is a colorless oil, of peculiar, not unpleasant odor and sharp acrid taste. The specific gravity at 25° was found to be 0.8509. It commences to boil at 202°, and the temperature slowly rises to 207°, after which it rises more rapidly, and a resinous mass remains in the flask.

On combustion:

I. 0.24725 gram oil gave 0.2723 gram H_2O and 0.7008 gram CO_2.

II. 0.2627 gram oil gave 0.2766 gram H_2O and 0.7483 gram CO_2.

III. 0.2064 gram oil gave 0.2193 gram H_2O and 0.5888 gram CO_2.

A sample of aldehyde was washed with dilute potassic hydrate to remove any acid possibly present from oxidation, and again dried. From this:

IV. 0.2184 gram oil gave 0.2369 gram H_2O and 0.6247 gram CO_2.

V. 0.2039 gram oil gave 0.2230 gram H_2O and 0.5825 gram CO_2.

	Calculated $C_{10}H_{18}O$.	I.	II.	III.	IV.	V.
C	77.92	77.29	77.68	77.80	78.00	77.91
H	11.69	12.23	11.69	11.80	12.05	12.14

The aldehyde is then isomeric with borneol and geraniol. The name *citronellic aldehyde* seems suitable as indicating its origin.

A vapor density determination by the method of Victor Meyer gave, D = 5.405: calc. = 5.34.

Citronellic aldehyde appears to be dextro-rotary: a column 2 decimeters long produces a deviation of about 7° for sodium light. Exact measurements are in progress.

The aldehyde readily absorbs bromine, the solution becoming warm. If the temperature rises too much, hydrobromic acid is given off and decomposition takes place. To determine the amount of bromine absorbed it was found convenient to weigh quickly about 1 gram of aldehyde, dissolve it in 20 cc. of chloroform or carbon disulphide, and run in, from a burette, a standardised solution of bromine in carbon disulphide, until a slight permanent red coloration was obtained. The bromine solution used contained 0.1163 gram bromine per cc. The following results were obtained:

I. 1.084 gram aldehyde required 9.0 cc. Br solution.
II. 1.885 gram aldehyde required 16.2 cc. Br solution.
III. 2.0149 grams aldehyde required 17.5 cc. Br solution.

Per cent. Br in bromo-derivative:

I.	II.	III.	Calculated Br_3.	Br_4.
49.1	49.9	50.3	50.9	67.5

These results, though only approximate, yet are sufficient to show that the unsaturation of the aldehyde is equivalent to two atoms of bromine.

Action of Heat on the Dibromide.

112 cc. of the bromine solution used above was gradually added to 12 grams of the aldehyde. The carbon disulphide was removed on a water-bath, and the residual liquid gradually heated to 120°, when torrents of hydrobromic acid were evolved. When this ceased, the residue was made alkaline and distilled with steam. The oil passing over was collected in ether, dried, and the ether driven off on a water-bath. A yellow oil amounting to 2 cc. was obtained, which possessed the odor of cymene, and on oxidation with hot permanganate solution yielded an insoluble acid, apparently terephthalic acid. This confirms Wright's statement; the reaction, however, is by no means quantitative.

Reduction of the Aldehyde.

25 grams aldehyde were mixed with 13 grams glacial acetic acid. 400 grams of 5 per cent. sodium amalgam were gradually added,

with occasional washing to remove the acetate formed. The resulting liquid was dissolved in ether, shaken up with bisulphite solution to remove any unchanged aldehyde, boiled with a little alkali to saponify any acetic ester possibly formed, washed, dried and distilled. The greater part boiled at 225°–230°. It gave no reaction with phenylhydrazine. It decolorised bromine solution, and possessed a pleasant odor of roses.

On combustion:

0.1972 gram oil gave 0.5550 gram CO_2 and 0.2299 gram H_2O.

	Calc. $C_{10}H_{20}O$.	Found.
C	76.92	76.75
H	12.82	12.95

This, then, is evidently the alcohol corresponding to citronellic aldehyde. On heating with acetic anhydride it yields a (probably) acetyl derivative, which has a curious quite characteristic odor.

Condensation Products.

Phenylhydrazine combines with the aldehyde very readily: on mixing the two liquids in equivalent proportions a turbidity soon appears, and a vigorous evolution of heat takes place. On chilling the resulting liquid, crystals soon form, and a semi-solid mass is obtained. The compound does not appear to be stable, however, as all attempts to isolate it in a crystalline condition were fruitless.

Aniline behaves similarly: the liquid product possesses a strong and rather disagreeable odor. Para-toluidine yields a similar compound. Attempts to prepare a condensation product with benzoic aldehyde were without result.

Acetyl chloride reacts vigorously with the aldehyde: the products have not yet been examined.

The acid corresponding to the aldehyde has not yet been obtained pure. Ordinary oxidising agents appear to split up the molecule, yielding fatty acids, etc. Potassium permanganate yields a mixture of acids, which smells strongly of ordinary valerianic acid.

Action of Phosphoric Anhydride on the Aldehyde.

Phosphoric anhydride acts very energetically upon citronellic aldehyde, and, unless kept cool, the liquid soon boils, and forms gummy products.

50 grams aldehyde were placed in a flask cooled by ice.

Phosphoric anhydride was added in small portions, with constant agitation, until no further heating occurred. The oxide was converted into a reddish curdy mass, and the liquid assumed a yellow tint. 200 cc. water and 100 cc. ether were now added, the mixture shaken well, and allowed to stand 24 hours. The liquid was then filtered from a white crystalline sediment, the yellow viscid ethereal solution separated from the watery layer, the latter again extracted with ether, and the combined ethereal solutions dried over calcium chloride. The ether was now removed on a water-bath and the residual oil fractioned. Between 140° and 180° a light oil passed over with some water. The temperature then rose rapidly to above 300°, when a thick oil passed over, which possessed a pleasant odor resembling the high-boiling fractions of citronella oil.

The light oil, after drying, was found to boil quite constantly at 175°–178°. It was heated with sodium for an hour on the water-bath, which produced a small brown precipitate.

On redistillation it boiled at 175°, and on combustion:

I. 0.1912 gram oil gave 0.2090 gram H_2O and 0.6125 gram CO_2.

II. 0.2343 gram oil gave 0.2556 gram H_2O and 0.7500 gram CO_2.

	Calc. $C_{10}H_{14}$.	$C_{10}H_{16}$.	Found. I.	Found. II.
C	89.55	88.23	87.36	87.29
H	10.44	11.76	12.14	12.13

This, then, is an impure terpene. To which class of terpenes it belongs has not yet been determined.

The white crystalline precipitate, filtered from the liquid containing the products of the action of phosphorus pentoxide, was washed with ether and dissolved in a little ether-alcohol, and allowed to crystallise. In 24 hours, large square colorless plates were deposited, which melt above 140°. The yield was about 2 grams. Another preparation furnished beautiful transparent prisms. They contain phosphorus, but have not yet been carefully examined.

Constitution of Citronellic Aldehyde.

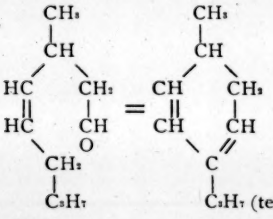
Although it may be a little premature to discuss the structure of this aldehyde, without more definite results, still the following considerations are of interest. By reason of its unsaturation the

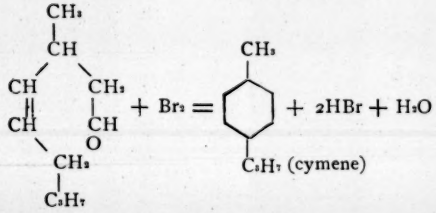
aldehyde cannot possess a "closed-chain" nucleus; moreover, none of its derivatives, except the phosphoric compound mentioned, have been induced to crystallise, while the closely related borneol and menthol series, which possess "ring" nuclei, crystallise readily.

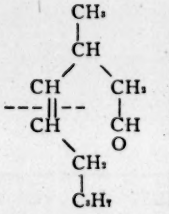
The easy conversion into a terpene and into cymene, and the very probable occurrence of valerianic acid among the oxidation products, are of great importance in fixing its structure.

The formula which most satisfactorily explains the chemical properties of the aldehyde is that of β-methyl δ-iso-butyl allyl-acetic aldehyde:

$C_4H_9—CH=CH—CH(CH_3)—CH_2—COH$:







On oxidation it should give valerianic and pyrotartaric acids, the latter of which would readily lose carbon dioxide and pass into butyric acid. The asymmetry of the β-carbon atom may account for its optical activity.

Much work, however, remains to be done before any formula can be assigned with certainty to the aldehyde.

Examination of the Constituent of b. p. 177°.

This oil is a light limpid liquid, having a very pleasant citrine odor. On combustion:

I. 0.2397 gram oil gave 0.2502 H_2O and 0.7444 gram CO_2.

II. 0.2695 gram oil gave 0.2854 H_2O and 0.8362 gram CO_2.

	Calc. $C_{10}H_{16}$.	I.	II.
C	88.23	84.8	84.6
H	11.76	11.6	11.7

The oil was evidently impure, and was distilled over sodium, which caused the separation of a dark flocculent precipitate. On combustion:

I. 0.1704 gram oil gave 0.1840 gram H_2O and 0.5377 gram CO_2.

II. 0.2049 gram oil gave 0.2176 gram H_2O and 0.6459 gram CO_2.

	Calc. $C_{10}H_{16}$.	I.	II.
C	88.23	86.05	85.90
H	11.76	11.9	11.7

These results are a little better, but it is evident that the oil retains a little of an oxygen compound very tenaciously. A vapor density determination by Meyer's method gave D = 4.96; calc. = 4.70.

The quantity of substance at my disposal was not sufficient to permit further treatment, and it was not possible to determine whether this terpene was identical with limonene, with which it agrees in boiling point. An attempt to prepare a solid tetrabromide was unsuccessful.

Examination of the Constituent of b. p. 222°.

This oil is a somewhat syrupy liquid, resembling in odor the citronellyl alcohol obtained by reduction of the aldehyde. On combustion:

0.2342 gram oil gave 0.2563 gram H_2O and 0.6693 gram CO_2.

	Calc. $C_{10}H_{18}O$.	$C_{10}H_{20}O$.	Found.
C	77.92	76.92	77.8
H	11.70	12.82	12.15

Its specific gravity at 26.5° was found to be 0.8741. This substance appears to have the properties of an alcohol. Acetic anhydride converts it into a product possessing the characteristic odor of the acetyl derivative of citronellyl alcohol. With sodium,

evolution of hydrogen occurs slowly in the cold, more rapidly on heating. The sodium compound is insoluble in ether, and when treated with acetyl chloride affords the same derivative as that obtained by direct action of acetic anhydride. These facts led me to doubt whether the composition $C_{10}H_{18}O$ could truthfully be assigned to this compound. In fact, remembering the tenacity with which the terpene retains traces of this oxygen compound, it seemed more than probable that the latter was equally contaminated with terpene, the result of which would be to raise the percentage of carbon.

Further, the occurrence of an aldehyde with an *isomeric* alcohol in an essential oil is quite anomalous, while numerous instances are known of aldehydes being accompanied by their *corresponding* alcohols.

To ascertain whether this was so, an attempt was made to purify the alcohol by means of the sodium compound. Sodium in small pieces was added to 10 grams of the supposed alcohol diluted with benzene, until no further evolution of hydrogen occurred on the water-bath. The pasty mass was then thoroughly pressed between filter papers and washed with ether. When dry it was suspended in water, decomposed by dilute hydrochloric acid, the separated oil collected in ether, and the ether solution dried and fractioned. An oil was obtained, boiling at 224°–226°. On combustion:

I. 0.2051 gram oil gave 0.2325 gram H_2O and 0.5648 gram CO_2.
II. 0.2378 gram oil gave 0.2610 gram H_2O and 0.6537 gram CO_2.

	Calc. $C_{10}H_{20}O$.	I.	II.
C	76.92	75.10	74.98
H	12.82	12.58	12.18

These results are far from satisfactory, yet it seems probable that the alcohol constituent of the oil is citronellyl alcohol, $C_{10}H_{20}O$.

The oil of tansy, examined by Bruylants,[1] bears a curious relation to oil of citronella. It was found to contain an aldehyde, $C_{10}H_{16}O$, the corresponding alcohol, $C_{10}H_{18}O$, and a terpene.

Examination of Other Grass Oils.

As far as I am aware, no extensive work has been published on oil of lemon-grass. Gladstone noted that it resembled citronella

[1] Ber. d. chem. Gesell. 11, 449.

very closely; Flückiger has observed its behavior with bisulphite solution. With the latter it reacts exactly like citronella; the aldehyde obtained appears to be quite different from citronellic aldehyde, and is now under investigation.

Oil of Turkish geranium has been carefully examined by Jacobsen,[1] who found it to contain a monatomic alcohol, geraniol, $C_{10}H_{18}O$.

Oil of ginger-grass has not yet been investigated. Oil of vetivert, by reason of its costliness, is somewhat difficult to work on. It appears to be quite different from all the other grass oils.

The study of these oils will be continued.

ORGANIC LABORATORY, SCHOOL OF MINES, N. Y., *Oct.* 1889.

Contributions from the Chemical Laboratory of the U. S. Department of Agriculture.

XIII.—THE MOLECULAR WEIGHTS OF CERTAIN SUBSTANCES AS INDICATED BY THE BOILING POINTS OF THEIR SOLUTIONS.

BY H. W. WILEY.

The apparatus with which the experiments to be described below were made, was devised in August of this year, and the experiments were commenced about the first of September. It was not my intention to publish the results of this work until they had been greatly extended, but the notice of the observations of Ernest Beckmann of his employment of the same method induces me to submit the data already obtained for publication.

I have no desire whatever to question Mr. Beckmann's priority in the use of the method, but it may be of interest to know that it was independently adopted by me, and all the data submitted below obtained before a notice of his work reached me in the *Chemisches Central-Blatt*, No. 7, 1889, this day received.

The apparatus employed consisted of an oval round-bottom flask, of about 200 cc. capacity, the neck of which was supplied with a side tube for the purpose of connecting it with an appropriate condenser. By this means the volume of the liquid employed was kept constant. The thermometer employed was accurately

[1] Ann. Chem. (Liebig), **157**, 232.

graduated to tenths, the distance between each tenth of a degree being so great that with the aid of the cathetometer used in reading it we could easily distinguish the .02 of a degree. The bulb of the thermometer was made to occupy the central portion of the liquid, the volume of which in all cases was 150 cc. To protect the bulb of the thermometer against the influence of the steam bubbles, it was covered with a double coating of fine copper foil. This method of coating the bulb of the thermometer of course precluded its use with substances easily reduced, such as silver and mercury salts.

Sodium chloride was the substance chosen to determine the factor for use. Carefully repeated determinations with this substance gave the following data: Substance taken, sodium chloride; volume of water, 150 cc.; weight of substance taken, 4.5 grams; weight of substance taken to 100 cc. of water, 3.0 grams; boiling point of water, 99.47°; boiling point of sodium chloride in solution, 99.93°; total rise of temperature, 0.46°; rise of temperature for 1 gram per hundred of substance, 0.1533°; molecular weight of sodium chloride, 58.5; factor $= 0.1533 \times 58.5 = 8.968$.

Using this factor as a constant, the following determinations have been made:

Substance taken.	Volume water.	Wt. substance taken in grams.	Wt. substance taken in grams to 100 cc. water.	Temperature of boiling water.
KCl	150	6.0	4.0	99.50
KBr	150	6.0	4.0	99.50
KI	150	9.0	6.0	99.50
KNO_3	150	6.0	4.0	99.50
$K_2Cr_2O_7$	150	18.0	12.0	99.50
$NaNO_3$	150	6.0	4.0	99.44
Sucrose	150	20.0	13.33	99.50
Oxalic acid	150	6.0	4.0	99.50

Substance taken.	Boiling temperature of solution of substance. C°.	Total rise of temperature. C°.	Calculated molecular weight.	Theoretical molecular weight.
KCl	99.85	.35	76.91	74.5
KBr	99.79	.29	123.7	119.0
KI	99.83	.33	163.1	166.0
KNO_3	99.83	.33	108.7	101.0
$K_2Cr_2O_7$	99.88	.38	283.2	295.0
$NaNO_3$	99.86	.42	85.4	85.0
Sucrose	99.70	.20	643.2	342.0
Oxalic acid	99.70	.20	179.4	90.0

In addition to the numbers given above, a large number of determinations have been made with substances containing water of crystallisation. In those cases the calculated molecular weight does not correspond either with the theoretical molecular weight, including the water of crystallisation, nor with the molecular weight of the anhydrous salt. These results seem to indicate that substances containing water of crystallisation exist in solution in a modified form, and the influence of this modification on the boiling point of the solution can only be determined by largely extended observations.

It is curious to note further, that in the two organic substances examined, the observed molecular weight obtained, using the same factor obtained by observations on the sodium chloride, is just about double the ordinary accepted molecular weight.

Since the factor for boiling solutions is so much less than that for the freezing mixtures, the determination of the molecular weight by the above method requires a solution considerably stronger than that used in Raoult's freezing method. The advantage, however, of having a mercurial column sensibly constant for long intervals of time renders it possible to make the observations with great accuracy.

To allow for the slight changes which take place in the boiling point of water under the conditions mentioned, I propose, hereafter, to use two pieces of apparatus, one of which shall contain water to be kept constantly in use, the observation of the boiling point of water and of the substance under examination being made at the same time. It is hardly necessary to mention that in such a case the thermometers employed would be carefully compared and the readings corrected accordingly. It is further necessary that the source of heat be sensibly constant, and we secure this by using a lamp with a certain sized flame, which remains unchanged throughout the whole series of observations.

For assistance in the analytical data obtained I am indebted to Mr. W. H. Krug.

WASHINGTON, D. C., *September* 14, 1889.

A RAPID METHOD FOR THE ESTIMATION OF SULPHUR IN ORGANIC COMPOUNDS.

By W. M. Burton.

The method here described is a modification of that proposed by Sauer,[1] which consists in burning the substance in a stream of oxygen, absorbing the sulphur dioxide in bromine water containing hydrochloric acid, and determining the sulphuric acid as barium sulphate.

The indicator tropaeolin 00, however, not being sensitive to carbonic acid nor to alkaline sulphites, it is practicable to absorb the sulphur dioxide in an excess of a standard solution of potassium hydrate, and titrate back the excess of alkali by means of a standard acid, using tropaeolin as an indicator. In this way the titration can be made almost immediately after the combustion is completed, thereby avoiding the tedious operation of evaporating the bromine and precipitating and weighing the barium sulphate, as is necessary in Sauer's method.

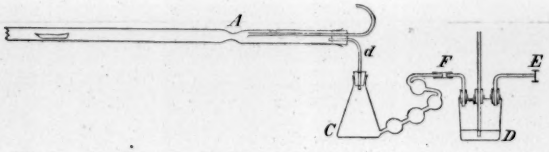
The Reagents.

1. A dilute aqueous solution of tropaeolin 00.

2. A standard solution of sulphuric acid of such strength that one cubic centimeter of it is equivalent to five milligrams of sulphur. Each cubic centimeter of such a solution would contain .015312 gram H_2SO_4.

3. A solution of potassium hydrate approximately equivalent to the sulphuric acid.

The Apparatus.



The combustion tube is arranged in the manner recommended by Sauer; the absorption apparatus is, however, somewhat mod-

[1] Ztschr. anal. Chem. **12**, 32 and 178.

ified, as shown in the accompanying figure. *C* is a flask with absorption bulbs containing the standard alkaline solution. Since the column of liquid in the bulbs exerts a pressure in the combustion tube sufficient to blow out the red-hot glass at *A*, it is necessary to relieve this by other means. This is accomplished by the three-necked bottle *D*, which contains a shallow layer of water, and is connected with the bulbs at *F* and with an aspirator at *E*. The degree of exhaustion is regulated by the screw-cock *E*, and increased or diminished pressure is indicated by the height of the water in the safety tube. It is recommended to maintain a slightly diminished pressure in the apparatus during the process of combustion.

Mode of Procedure.

An amount of alkali equivalent to fifteen cubic centimeters of the standard acid is measured into the absorption bulbs; distilled water is added until an amount of liquid is present sufficient to fill the first three bulbs. Any excess of water should be avoided, in order to prevent the alkaline solution from being drawn over into the bottle *D*. The apparatus is then arranged as indicated in the figure, *A* is heated red hot, and the combustion is carried out in the manner recommended by Sauer. After the substance has been completely burned, the tube is swept out by means of a current of air or oxygen, and the apparatus is allowed to cool.

The combustion tube, the inlet tube for the oxygen, and the connecting tube *d* are rinsed with water to remove traces of sulphur dioxide or sulphur trioxide, and the rinsings are added to the liquid in the bulbs. A few drops of the tropaeolin solution are then added, and the excess of alkali titrated directly in the absorption bulbs. The change of the colored solution from yellow to red is quite sharp and distinct, allowing very close titration. The accuracy of the method was tested by determining the sulphur in samples of pure para-toluene-sulphamide, ortho-sulpho-benzoic acid and its acid ammonium salt. The results are given below.

Toluene-sulphamide (p).

Theoretical percentage of sulphur in $C_6H_4 < \begin{matrix} CH_3 \\ SO_2NH_2 \end{matrix}$ (*p*), 18.71.

Found: 18.90, 18.86, 18.65, 18.79, 18.80.

Ortho-sulpho-benzoic Acid.

Theoretical percentage of sulphur in $C_6H_4 < \begin{matrix} COOH \\ SO_2OH \end{matrix} (o) + 4H_2O$, 11.68.

Found: 11.50, 11.60, 11.55, 11.62, 11.57.

Acid Ammonium Salt.

Theoretical percentage of sulphur in $C_6H_4 < \begin{matrix} COOH \\ SO_2ONH_4 \end{matrix} (o)$, 14.61.

Found: 14.75, 14.81, 14.70, 14.68, 14.83.

The sulphur in a sample of crude petroleum was also determined by this method. As the percentage of sulphur in the oil was small, the standard solutions were diluted five times. The quantity of sulphur in the oil was also estimated by Carius' method. The results are given below:

By Carius' method: .53, .50, .48 per cent. S.

By method here described: .50, .49, .49 per cent. S.

It is, of course, evident that the sulphur in carbon compounds containing any of the halogens, phosphorus, or arsenic, could not be determined by this method, as there would be other acids formed which would vitiate the results.

CLEVELAND, *October*, 1889.

THE ACTION OF LIGHT ON SILVER CHLORIDE.[1]

BY ROMYN HITCHCOCK.

The plan of investigation, the first results of which I have the honor to bring before you at this time, was proposed by me in May, 1885. Since then I have mentioned the method several times in conversation, but it is only recently that I have been able to put it to a practical test.

The single set of experiments here described are only preliminary to a more thorough examination of the action of light, which, it is hoped, may be carried out in future. This includes a study of—

[1] Read before the Chemical Section of the A. A. A. S., Toronto, 1889.

1. The action of light upon chemically pure haloids of silver.

2. The conditions which favor the decomposition of such compounds by light.

3. The products of the decomposition.

4. The activity of different parts of the spectrum in effecting the decomposition.

The subject is one which has been much studied, but we have scarcely more definite knowledge of the chemical effect of light upon the silver haloids now than was possessed in the time of Scheele, in 1777. I have been carefully over most of the literature of the subject, and it is quite extensive, but the results are confusing and contradictory. Even such an apparently simple question as whether there is a loss in weight when silver chloride is exposed to light, has only been satisfactorily settled by the recent work of Prof. Spencer Newberry. Yet the fact that chlorine is set free by the action of light was conclusively proved by Scheele, and that the quantity set free is not inconsiderable is evident from the strong odor observed.

I will not detain you by reviewing even the more important experiments recorded in the past, but will pass on to the considerations which led me to adopt a different method of experimenting. Recognising that there must either be a loss in weight corresponding to the weight of chlorine set free, or else that the chlorine must be replaced by some other element, it seemed quite plausible that an oxychloride might be formed by the action of light, as has been suggested by different writers. If two atoms of oxygen should take the place of one atom of chlorine in some unaccountable manner, then no appreciable change in weight would result. Seebeck and Abney have observed that silver chloride is not acted upon by light except in the presence of moisture, and Hodgkinson concluded that an oxychloride was formed, from which he obtained a small quantity of oxygen by heating it in an exhausted tube. This experiment, and those of Dr. W. Schmid[1] on the decomposition of plumbic iodide by light, seemed to lend strength to a rather improbable hypothesis.

Nevertheless, the subject seemed to deserve a more critical examination, and I determined as the first step not only to weigh the chloride before and after exposure to light, but also to determine the amount of chlorine set free. If an oxychloride is

[1] Pogg. Ann. 127, 7 (1866), 493.

formed, the weight of chlorine set free must exceed the loss in weight of the chloride.

But the discrepancies in the results of observations on the loss in weight were too great to be overlooked. Why, for example, should von Bibra find that there is no loss in weight, while Prof. Newberry found a very considerable change? I will answer this question as we go on. First, I wish to remind you of von Bibra's method of working. He filled small watch-glasses with white chloride and exposed them to sunlight under bell-jars for five weeks, the chloride being occasionally stirred to expose fresh surfaces. No loss in weight could be detected. The darkened product yielded no silver to nitric acid, but ammonia dissolved the greater part of it, leaving a residue soluble in nitric acid.

In thinking over the subject I became convinced that in all experiments up to this time the action of light upon the chloride has been only superficial. The energy required to effect the separation of the haloid must be considerable, for, as Draper showed long ago, even the thin film of a daguerreotype plate absorbed the active rays so effectually as to render a beam reflected from one sensitised surface inactive upon another. It therefore became necessary to obtain the chloride in a very finely divided condition, in order to ensure the complete action of the light upon it.

To accomplish this result a number of thin slips of glass, such as are used for cover-glasses in mounting microscopical specimens, were numbered with a diamond, cleaned by boiling in nitric acid, washed, and placed in a desiccator over sulphuric acid. These were accurately weighed, and I may here state that throughout these experiments two, and usually three independent weighings, on different days, were made for each operation. These slips were placed on strips of glass lying on the bottom of a crystallising jar. A very dilute solution of silver nitrate was then precipitated with chlorhydric acid in a beaker, and while the glass slips were held in place, this milky liquid was poured over them. The jar was set aside in a dark closet until the precipitate had deposited. The supernatant liquid was very slowly drawn off with a siphon, and distilled water run in by the same means. The deposited chloride is extremely light and the slightest current in the water will wash it from the glasses. The siphon must therefore have one end drawn out to a rather small point, so that it shall act very slowly. This washing by decantation must be repeated many

times on successive days, in order to allow the salts in solution to diffuse thoroughly through the water, for it is not safe to draw off the water entirely, leaving the surfaces of the slips uncovered. Finally the water was drawn off as perfectly as possible, and the jar set aside until the remaining water had evaporated and the slips were quite dry. They were then picked out with forceps and placed in a desiccator, where they were allowed to remain several days or a week. They were then weighed. All these operations were done by artificial light. Slips thus prepared have a beautifully even, translucent coating of white silver chloride. Print can be read through them with ease. The slips measured about ¾-inch in width by 1½ inches in length.

The slips were placed in a glass tube, drawn off at one end to receive a rubber connection from a set of bulbed U-tubes containing a solution of silver nitrate. The other end was closed with a tubulated rubber cork and connected with a hydrogen apparatus. The hydrogen was passed through silver nitrate before it entered this tube. The tube was long enough to take four slips. When all was ready the apparatus was set out on the top of the National Museum in bright sunlight at 11.15 A. M., August 19th, and kept running until 4.30 P. M., when the slips were returned to the desiccator, and the tube and U-tubes washed out into a beaker. It should be stated that the U-tubes were shielded from the light during the experiment by a covering of black paper.

The silver chloride from the U-tubes was determined by collecting it in a porcelain crucible. After the slips had remained over night in the desiccator they were weighed, and the next day weighed again. The results are given in full in the following table I.

SUMMARY OF RESULTS.

I. *From Hydrogen Apparatus.*

No.	Wts. of Slips.	Slips + AgCl.	Wt. of AgCl.	Slips exposed.	Loss.
1	Not used.				
2	.49575	.51870	.02295	.51775	.00095
3	.45840	.47420[1]	.01580	...	...
4	.45563	.48350	.02787	.48225	.00125
5	.49955	.52405	.02450	.52285	.00120
6	.44163	.46575	.02412	.46460	.00115
7	.38590	Lost	...	...	...
8	.33080	.35370	.02290	...	...

[1] This slip was not more than two-thirds covered, as it was displaced in the precipitating jar and slid partly under one of the other slips.

The amount of chlorine set free by the action of light was found to be somewhat less than the total loss in weight of the four slips used, but allowing for experimental errors, the discrepancy is not considerable. I am confident that a closer agreement will be observed in future experiments. The results were:

Weight of crucible + AgCl,	4.0143
" " "	3.9982
" " AgCl,	0.0161
Chlorine collected,	0.0040
Total loss in weight of slips,	0.0045

Prof. Newberry dissolved a quantity of silver nitrate corresponding to 0.1 gram of chloride in water and precipitated the chloride with sodium chloride. The precipitate was exposed to direct sunlight while a current of air was passed through the liquid. The precipitate was then weighed on a Gooch filter. From preliminary experiments he found that the precipitated chloride, before exposure to light, weighed .0996 to .0997 gram instead of 0.1000 gram. The metallic silver was weighed after dissolving out the chloride on the filter with ammonia. His results are thus given after exposure to sunlight:

	Weight.	Loss.	Met. Ag.	Met. Ag calc. from loss.
1	.0967	.0029	.0054	.0085
2	.0979	.0018	.0076	.0054
3	.0969	.0027	.0078	.0081
4	.0982	.0015	.0062	.0045

Placing the results of Prof. Newberry's experiments and of my own side by side, and reducing them both to represent the loss in weight of .1 gram of silver chloride, we have these figures:

		Loss.	
	Weight of AgCl.	Newberry.	Hitchcock.
1	0.1000 gram.	.003	.00418
2	0.1000	.0018	.00448
3	0.1000	.0027	.00490
4	0.1000	.0015	.00485

Two slips prepared as above, numbered 3 and 8 in table I, were exposed under a beaker-cover, without a current of gas or any attempt to collect the chlorine set free. The dry chloride taken

from the desiccator was scarcely discolored in an hour in bright sunlight. A drop of distilled water on one of the slips caused immediate discoloration in the sunlight, confirming the idea that moisture is necessary for the reaction. The discoloration went on more slowly than in the hydrogen apparatus, and the exposure was continued for two days. The results show that in my experiments with the hydrogen apparatus the decomposition was not complete. The experiment should have continued over two days. It will be a matter of subsequent experiment to determine how long the action of light must continue to ensure its full effect.

The results of this last experiment are as follows:

No.	Glass.	Glass + AgCl.	Wt. of AgCl.	After Exp.	Loss.	Calc. for .1 gram.
3	.4584	.4742	.0158	.47325	.00095	.0060
8	.3308	.3537	.0229	.35230	.0014	.0062

It would appear that while the limit of the action of light may not have been reached even in the last experiments, the action proceeds regularly and is proportionate to the duration of the exposure, when the chloride is thus finely divided.

It will be obvious, from a consideration of the figures, that the results cannot be accepted as final, for it is doubtful whether the product representing the ultimate action of light has yet been obtained. It has not been deemed profitable to speculate upon the composition of such a product at this stage of the experiments.

I would state, however, that the product of the action of light in one experiment (slip No. 3) gave up a very considerable portion of silver when heated with dilute nitric acid. This fact, so directly opposed to all previous results, conclusively shows that the action of the light in these experiments has proceeded further among the particles than in those performed in the usual manner with the chloride in mass. The presumed protective action of a large excess of unchanged chloride upon the product of the reduction is to a great extent eliminated, and we find that product to be readily soluble. The bearing of this fact upon the sub-chloride hypothesis, and also upon the researches of M. C. Lea on his photo-salts of silver, is obvious.

Perhaps more may justly be claimed for the method than for the few preliminary results. I see no reason why the method should not lead to a solution of the problem of the action of light on the haloids of silver. We may thus accurately determine:

1. The loss of weight when light has fully acted on the compound.

2. The weight of the haloid set free by that action.

From these results one can readily determine whether or not the action is merely a setting free of the haloid, or the formation of a compound of silver with some other element, as oxygen for example, at the same time. The results already obtained clearly show, to my mind, that there is no such double decomposition, but they must yet be verified. Water seems to be necessary to the reaction, but it probably does not suffer decomposition.

In conclusion, I would express my indebtedness to Prof. F. W. Clarke, Chief Chemist of the Geological Survey, for affording me the laboratory facilities for carrying on this work, and also to Dr. Carl Barus for the use of the fine Bunge balance belonging to the physical laboratory of the Survey, on which all the weighings were made.

WASHINGTON, D. C., *August* 23, 1889.

REVIEWS AND REPORTS.

ON THE CONSTITUTION OF HYDROXYLAMINE AND ITS DERIVATIVES.

The discovery of hydroxylamine among the reduction products of nitric acid, by Professor W. Lossen,[1] in 1865, was not only of great theoretical interest, on account of the light which it threw upon the nature of this reduction, but it also enriched chemical science with a substance which was found to have most interesting and valuable properties. Hydroxylamine, as is well known, has become in recent years a most useful reagent for studying the structure of organic compounds. Its derivatives constitute several new and important classes of compounds. For example, the ease with which it reacts with substances containing the carbonyl group, $=CO$, has given rise to the formation of the compounds known as *oximes*, which are characterised by the group $=CNOH$. So also the nitriles, compounds containing the cyanogen group $-CN$, combine directly with hydroxylamine and form the so-

[1] Ann. Chem. (Liebig), Suppl. Bd. 6, 220.

called *amidoximes*, compounds which contain the group $-C<^{NH_2}_{NOH}$.

On the other hand, owing to the readiness with which it can be decomposed and the nature of its decomposition products, hydroxylamine is used in inorganic chemistry as a powerful reducing agent. By means of it many metals, such as gold, silver, palladium, and mercury, can be precipitated in pure condition from solutions of their salts.

Ever since he discovered the compound Professor Lossen has carried on an investigation, the object of which has been to determine experimentally the structural formulas of hydroxylamine and its derivatives. As the compound is obtained by the reduction of nitric acid, and its composition is expressed by the formula NH_3O, the simplest conception of its constitution is to regard it as a substitution product of ammonia in which one hydrogen atom has been replaced by hydroxyl, thus,

$$H-O-N<^{H}_{H}.$$

Its formation from nitric acid would then be represented by the equation

$$H-O-NO_2+6H=H-O-NH_2+2H_2O.$$

This equation is analogous to that which represents the formation of amine bases from nitro compounds,

$$R-NO_2+6H=R-NH_2+2H_2O,$$

and, like the amines and ammonia, hydroxylamine unites directly with acids to form salts. These facts are in accordance with what would be expected of a compound having the structure represented above, but it is also evident that all the hydrogen atoms are not of equal value in this formula. Two of them are of equal value and bear the same relation to the nitrogen atom, but the third bears a different relation to the nitrogen; it is intimately associated with oxygen. From such a compound different substitution products should be obtained accordingly as the substituting group replaces the hydrogen of the hydroxyl group, or the hydrogen of the amido group. The plan of Lossen's work was to make substitution products of hydroxylamine, and by a comparison of their properties he hoped to get experimental evidence either for or against the formula.

In the first place he found[1] that substitution products of hydroxylamine can be prepared by the same methods that are used for making substitution products of ammonia. Thus when acid chlorides are treated with ammonia, acid amides are obtained, for example,

$$\underset{\text{Benzoyl chloride.}}{C_7H_5OCl}+2NH_3=\underset{\text{Benzamide.}}{C_7H_5ONH_2}+NH_4Cl.$$

[1] Ann. Chem. (Liebig) **161**, 347.

In like manner acid chlorides and hydroxylamine give the so-called *hydroxamic acids.*

$$\underset{\text{Benzoyl chloride.}}{C_7H_5OCl} + 2NH_2OH = \underset{\text{Benzhydroxamic acid.}}{C_7H_5ONH_2O} + NH_2O.HCl.$$

Other hydroxamic acids were prepared by Lossen[1] in a similar manner, and the conclusion appeared justified that the hydroxamic acids bear the same relation to hydroxylamine that the acid amides bear to ammonia. By further treatment of the hydroxamic acids with acid chlorides a second and third acid group can be introduced into the compound. Thus benzhydroxamic acid on treatment with benzoyl chloride gives dibenzhydroxamic acid, and finally tribenzhydroxylamine. By simple reactions, as, for example, boiling with dilute hydrochloric acid, these substituting groups can be again eliminated from the compound.

In the early stages of the investigation[2] a large number of these hydroxamic acids were prepared and studied. It was soon observed that the disubstitution products exist in two isomeric conditions, and this fact is in accordance with the formula for hydroxylamine, there being two kinds of hydrogen atoms in the compound. But on examining the trisubstitution products, most remarkable and unexpected results were obtained;[3] thus tribenzhydroxylamine, made by replacing all of the hydrogen atoms with benzoyl groups, was obtained in three metameric forms, whereas theoretically but one such compound is possible. So also trisubstitution products containing two different groups were found to exist in more forms than are theoretically possible. Thus two dibenzanisylhydroxylamines are theoretically possible having the formulas

$$\left.\begin{matrix}C_7H_5O\\C_7H_5O\end{matrix}\right\rangle N-O-C_8H_7O_2 \text{ and } \left.\begin{matrix}C_8H_7O_2\\C_7H_5O\end{matrix}\right\rangle N-O-C_7H_5O,$$

but it was found that three such compounds exist, each of which differs from the others in its properties.

A large number of other instances were noticed in which the number of isomeric compounds found was in excess of the number theoretically possible, and while in some cases it seemed probable that one and the same compound could exist in more than one physical modification, nevertheless the hypothesis of physical isomerism could not account for all the facts observed. Lossen finally reached the conclusion[4] that each of the three hydrogen atoms of hydroxylamine has a different value from the others, and further that each separate affinity of one and the same nitrogen atom may under certain circumstances act in a different manner from the others.

This conclusion rests primarily upon the assumption that the

[1] Ann. Chem. (Liebig) **178**, 213. [2] Ibid. **175**, 282. [3] Ibid. **178**, 225.
[4] Ibid. **186**, 1; **186**, 55.

behavior of hydroxylamine and of ammonia towards acid chlorides is analogous, that substitution products of one are formed in the same way as are those of the other; that in the formation of benzhydroxamic acid, for example, the acid group benzoyl is present in the compound as a univalent group, thus $(C_7H_6O)H_2NO$, just as in benzamide the benzoyl group is in combination with the amido group $(C_7H_5O)NH_2$. This assumption appeared justified because the acid groups could again be eliminated unchanged from the molecule by the simplest reactions, and indeed no other method of explaining the action seemed possible at the time.

A more accurate knowledge of the behavior of hydroxylamine and the nature of its derivatives resulted from the study of the action of this substance upon aldehydes and ketones. Victor Meyer[1] and his co-workers carried out a series of important investigations upon the aldoximes and ketoximes, and came to the conclusion that the mode of action of hydroxylamine and ammonia is totally different. It was found that while ammonia in forming amido compounds must be present in the free condition and in concentrated solution; hydroxylamine, on the other hand, formed derivatives when present in extremely dilute solution and even when present as a salt. These and other investigations, especially those of Wallach, and Pinner upon the amidines, led Lossen finally to the view[2] that when acid chlorides and esters act upon hydroxylamine, the action takes place differently from that which obtains in the case of acid chlorides and esters acting upon ammonia. That benzhydroxamic acid, for example, instead of being a mono-substitution product of hydroxylamine, $\begin{matrix} C_7H_5O \\ H \end{matrix}\!\!>\!NOH$, must be considered as a benzenyl compound having the structure

$$C_6H_5-\underset{\displaystyle OH}{\underset{|}{C}}=NOH .$$

If the latter formula is the correct one for benzhydroxamic acid, then the difficulty of accounting for the numerous isomeric hydroxylamine derivatives disappears to a great extent. On the other hand, the formation of the compound by the action of benzoyl chloride upon hydroxylamine cannot be so easily expressed. The more recent investigations of Lossen[3] have brought more and more evidence in favor of the latter formula, so that at the present time he regards it as the only tenable one.

This view is based upon the following reasons: If benzhydroxamic acid is a benzenyl compound having the constitution represented by the formula $C_6H_5-C\begin{matrix} \nearrow NOH \\ \searrow OH \end{matrix}$, then it ought to be possible to prepare it by simple reactions from benzenyl compounds; and if

[1] Ber. d. deutsch. Ges. **15**, 2787. [2] Ibid. **16**, 873. [3] Ann. Chem. (Liebig) **252**, 170.

in addition to this it is possible to effect the reverse change, that is, transform benzhydroxamic acid into benzenyl derivatives, then the formula may be regarded as proved. Both of these changes have been effected. In the first place, ethyl benzhydroxamic acid, an easily prepared derivative of benzhydroxamic acid, has been made by starting with benzimido ether. Benzonitrile in uniting with alcohol forms benzimido ether, and the latter substance by the action of hydroxylamine is converted into ethyl benzhydroxamic acid according to the equation:

$$\underset{\text{Benzimido ether.}}{C_6H_5C\begin{matrix}=NH\\ \diagdown OC_2H_5\end{matrix}} + H_2NOH.HCl = \underset{\text{Ethyl benzhydroxamic acid.}}{C_6H_5C\begin{matrix}=NOH\\ \diagdown OC_2H_5\end{matrix}} + NH_4Cl.$$

On heating the hydrochloric acid salt of ethyl benzhydroxamic acid, benzhydroxamic acid itself is obtained.

Secondly, the ethyl ester of benzhydroxamic acid has been prepared from benzenylamidoxime. The latter substance is formed by the action of hydroxylamine upon benzonitrile, and its structural formula as determined by Tiemann and Krüger[1] is $C_6H_5C\begin{matrix}=NOH\\ \diagdown NH_2\end{matrix}$. By the action of ethyl iodide upon the sodium compound of this substance the ethyl ether is obtained, $C_6H_5C\begin{matrix}=NOC_2H_5\\ \diagdown NH_2\end{matrix}$. If the hydrochloric acid salt of this ether be treated with nitrous acid, benzenylethoxime chloride is formed, a substance having the formula $C_6H_5C\begin{matrix}=NOC_2H_5\\ \diagdown Cl\end{matrix}$. This chloride with sodium ethylate yields the ethyl ester of ethyl benzhydroxamic acid $C_6H_5C\begin{matrix}=NOC_2H_5\\ \diagdown OC_2H_5\end{matrix}$, and the hydrochloric acid salt of the latter when heated gives the ethyl ester of benzhydroxamic acid.

Tiemann and Krüger,[2] who first studied the action of nitrous acid upon benzenylamidoxime ethyl ester, expected to get, as the immediate product of the action, benzhydroxamic acid ethyl ester according to the equation:

$$\underset{\text{Benzenylamidoxime ethyl ester.}}{C_6H_5C\begin{matrix}=NOC_2H_5\\ \diagdown NH_2\end{matrix}} + HCl + NaNO_2 =$$

$$NaCl + N_2 + H_2O + \underset{\text{Benzhydroxamic acid ethyl ester.}}{C_6H_5C\begin{matrix}=NOC_2H_5\\ \diagdown OH\end{matrix}}.$$

As they obtained the chloride $C_6H_5C\begin{matrix}=NOC_2H_5\\ \diagdown Cl\end{matrix}$, and since this chloride cannot be formed by the direct action of hydrochloric acid upon benzhydroxamic acid ethyl ester, they conclude that the immediate product of the action, a compound which must

[1] Ber. d. deutsch. Ges. **17**, 1691. [2] Ibid. **18**, 727.

have the constitution $C_6H_5C\overset{NOC_2H_5}{\underset{OH}{<}}$, cannot be identical with benzhydroxamic acid ethyl ester, and therefore benzhydroxamic acid cannot have the formula $C_6H_5C\overset{NOH}{\underset{OH}{<}}$. Lossen, however, in his last paper,[1] refutes this interpretation of the reaction, and maintains that the reaction takes place according to the equations:

$$C_6H_5C\overset{NOC_2H_5}{\underset{NH_2}{<}} + HCl + NaNO_2 = C_6H_5C\overset{NOC_2H_5}{\underset{N_2.OH}{<}} + H_2O$$

$$C_6H_5C\overset{NOC_2H_5}{\underset{N_2OH}{<}} + HCl = C_6H_5C\overset{NOC_2H_5}{\underset{Cl}{<}} + N_2 + H_2O.$$

And as the chloride thus obtained can be converted into benzhydroxamic acid, it again proves that the latter is a benzenyl compound.

The reverse change, namely, the transformation of benzhydroxamic acid into benzenyl compounds, has been effected in several ways. The ethyl ester of benzhydroxamic acid by the action of ethyl iodide and caustic potash is converted into ethyl benzhydroxamic acid ethyl ester:

$$C_6H_5C\overset{NOC_2H_5}{\underset{OH}{<}} + KOH + C_2H_5I =$$

$$C_6H_5C\overset{NOC_2H_5}{\underset{OC_2H_5}{<}} + KI + H_2O.$$

Ethyl benzhydroxamic acid ethyl ester.

But the latter substance is a benzenyl compound which has been made by the action of sodium ethylate upon benzenylethoxime chloride. Further, the ethyl ester of benzhydroxamic acid can be directly converted into benzenylethoxime chloride by treatment with phosphorus pentachloride.

$$C_6H_5C\overset{NOC_2H_5}{\underset{OH}{<}} + PCl_5 = C_6H_5C\overset{NOC_2H_5}{\underset{Cl}{<}} + POCl_3 + HCl.$$

Benzhydroxamic acid ethyl ester. Benzenylethoxime chloride.

In a similar manner ethyl benzhydroxamic acid ethyl ester can be converted into the same chloride. But this chloride is undoubtedly a benzenyl compound, because it can be prepared by the action of nitrous acid upon benzenylamidoxime ethyl ester.

Ethyl benzhydroxamic acid has also been converted into benzenylamidoxime by the action of ammonia according to the equation:

$$C_6H_5C\overset{NOH}{\underset{OC_2H_5}{<}} + NH_3 = C_6H_5C\overset{NOH}{\underset{NH_2}{<}} + C_2H_6O.$$

Ethyl benzhydroxamic acid. Benzenylamidoxime.

and the ethyl ester of the acid, by similar treatment, gives the ethyl ester of benzenylamidoxime.

[1] Ann. Chem. (Liebig) **252**, 181.

The results of the investigation may also be expressed in this way: The compounds benzhydroxamic acid, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NOH\\ \diagdown OH\end{matrix}$, ethylbenzhydroxamic acid, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NOH\\ \diagdown OC_2H_5\end{matrix}$, benzenylethoxime chloride, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NOC_6H_5\\ \diagdown Cl\end{matrix}$, and benzenylamidoxime, $C_6H_5C\begin{matrix}\diagup\!\!\diagup NOH\\ \diagdown NH_2\end{matrix}$, can be readily transformed, by means of clean reactions, one nto another, and the simplest explanation of their relationship is that they are all benzenyl compounds, as indicated by the formulas.

Benzhydroxamic acid being, therefore, a benzenyl compound, its formation from benzoyl chloride and hydroxylamine cannot be r presented by the simple equation given above, but must be e pressed by some such equations as the following:

$$C_6H_5C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown Cl\end{matrix} + NH_2OH = C_6H_5C\begin{matrix}\diagup OH\\ -NHOH\\ \diagdown Cl\end{matrix}$$

$$C_6H_5C\begin{matrix}\diagup OH\\ -NHOH\\ \diagdown Cl\end{matrix} = C_6H_5C\begin{matrix}\diagup\!\!\diagup NOH\\ \diagdown OH\end{matrix} + HCl$$

according to which the hydroxylamine at first forms an addition product which immediately breaks up into hydroxamic acid and hydrochloric acid.

The constitution of benzhydroxamic acid having been determined, that of the other hydroxamic acid can be readily understood. Thus, by further action of benzoyl chloride, dibenzhydroxamic acid, a compound having the formula $C_6H_5C\begin{matrix}\diagup\!\!\diagup NO(COC_6H_5)\\ \diagdown OH\end{matrix}$ is obtained. And in a similar manner the constitution of the three isomeric dibenzanisylhydroxylamines is represented by the formulas:

$C_6H_5C(OCOC_7H_7O)=NO(COC_6H_5)$ dibenzanishydroxylamine,
$C_6H_5C(OCOC_6H_5)=NO(COC_7H_7O)$ benzanisbenzhydroxylamine,
$C_7H_7OC(OCOC_6H_5)=NO(COC_6H_5)$ anisdibenzhydroxylamine.

In this manner nearly all the cases of isomerism,[1] which in the earlier stages of the investigation seemed so inexplicable, can be accounted for, and no facts are at present known which indicate that the formula of hydroxylamine is different from that ordinarily assigned to it. The investigation is not yet finished, a number of the hydroxylamine derivatives exist in more than one physical modification, and a careful study is now to be made of the behavior and transformations of these substances. The phenomena of physical isomerism are receiving at present a great deal of attention from chemists, and Prof. Lossen thinks that it may be possible to explain the nature of these hydroxylamine derivatives by means of tereometric formulas.

E. H. Keiser.

[1] Ann. Chem. (Liebig) **252**, 195.

ON THE CONSTITUTION OF BENZENE.

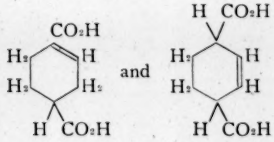
Since Kekulè's theory was proposed there has been, until recently, but little advance in our knowledge of the real constitution of benzene. The "ortho," "meta" and "para" positions have been established for groups in thousands of compounds, but these compounds can be equally well explained by the formula of Kekulè, of Claus, of Dewar, or of Ladenburg.

It would seem that the only means which can furnish a solution of the problem is a study of the transformation of members of the marsh gas series into benzene derivatives, or vice versa.

With this thought in mind, Baeyer[1] has shown that the quinone-hydro-dicarbonic ester obtained by Herrmann[2] from succinylo-succinnic ester is identical with the ester of dioxyterephthalic acid, and that it can be transformed into terephthalic acid. This furnishes a transformation of a hexamethylene derivative into a benzene derivative, and gives the first satisfactory refutation of Ladenburg's prism formula. A consideration of the prism formula shows that in the transformation into hexamethylene, only *one* of the three para positions can remain para, and the other two must become ortho. But in the transformation referred to, *two* pairs of groups in the para position remain para. This can be explained by Ladenburg's formula only by supposing such a wandering of groups from one position to another as is, to say the least, very improbable.

An extended study of succinylo-succinnic acid is difficult, owing to the ease with which it is decomposed. This led Baeyer[3] to take up, instead, the study of the reduction products of terephthalic acid.

To render more clear what follows, a few words must be said upon the nomenclature proposed for the hydro-terephthalic acids. The Greek letter Δ is used to represent a double union, and a numeral following it indicates the carbon atom from which the double union begins when passing around the ring in the direction in which the carbon atoms are numbered. Thus the two acids:



would be

Δ^1 tetrahydro-terephthalic acid,
and Δ^2 " " "

In the case of "geometric" isomers, to avoid the somewhat

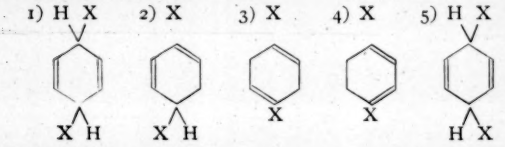
[1] Ber. d. chem. Ges. **19**, 428. [2] Ann. Chem. (Liebig) **211**, 327.
[3] Ibid. **245**, 103, and **251**, 257.

cumbersome terms fumaroid and maleïnoid, it is proposed to give compounds having groups on the same side of the plane of the ring the prefix "cis," while compounds having groups on opposite sides of the plane of the ring are called "cistrans." To indicate this kind of isomerism the Greek letter *I* is used. This nomenclature can be applied, also, to such compounds as fumaric and maleic acids, and, by use of the signs + and — (instead of cis, etc.), to the tartaric acids.

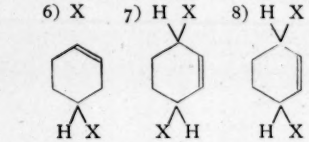
A consideration of the structure of the hydro-terephthalic acids leads us to expect ten such acids. These have all been obtained by Baeyer, and the structure of each ascertained with a high degree of probability.

These acids are:

a. Dihydro-terephthalic acids.

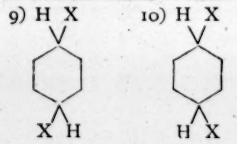


b. Tetrahydro-terephthalic acids.



1) $\Delta^{2.5}I^{cistrans}$
2) $\Delta^{1.5}$
3) $\Delta^{1.4}$
4) $\Delta^{1.3}$
5) $\Delta^{2.5}I^{cis}$
6) Δ^{1}
7) $\Delta^{2}I^{cistrans}$
8) $\Delta^{2}I^{cis}$

c. Hexahydro-terephthalic acids.



9) $I^{cistrans}$
10) I^{cis}

The dihydro acids 1) and 5) are formed when terephthalic acid is reduced by sodium amalgam, the mixture being vigorously shaken and cooled, and carbon dioxide being passed through the solution to prevent the action of free alkali.

The proofs for the structure are:

1. Of the dihydro acids, only the $\Delta^{2.5}$ acid can exist in forms which are geometric isomers.

2. The acid takes up directly four atoms of bromine.

3. The acid contains two hydrogen atoms very loosely held in the molecule, the methyl ester losing hydrogen and being converted entirely into the ester of terephthalic acid merely by heating on the water-bath. The esters of the other dihydro acids do not conduct themselves in this way. Permanganate in alkaline solution oxidises the acid to terephthalic acid. This is not the case with the other acids. This is explained by the position of the two double unions which, by their negative nature, give to the hydrogen atoms the same mobility which we find in aceto-acetic ether and benzyl cyanide where a methylene group is situated between two negative groups.[1]

4. The acid is changed into the $\Delta^{1.5}$ acid by boiling the aqueous solution, and into the $\Delta^{1.4}$ acid by boiling with caustic soda. It has been shown in the case of hydro-muconic acid that such treatment causes a double union to shift from the $\beta\gamma$ to the α,β position, and such a shifting can take place *twice* only with the $\Delta^{2.5}$ acid.

5. The acid is not further reduced by sodium amalgam in the cold, while each of the other acids is so reduced. It is found in other cases that a double union adjacent to the carboxyl group is much more easily reduced than a double union in the $\beta\gamma$ position.

The geometric isomers of the $\Delta^{2.5}$ acid are distinguished by their different solubilities, the *l*-[cis- and trans-] acid being much more difficultly soluble than the other.

The $\Delta^{1.5}$ dihydro-terephthalic acid is obtained by boiling the $\Delta^{2.5}$ acid with water. This method of preparation, taken in connection with what has been said, gives one proof of the structure of the acid. A second proof is that sodium amalgam reduces the acid to the Δ^{2} tetrahydro acid. This is probably caused by the proximity of one double union to a carboxyl group, the latter by its negative character rendering the addition of hydrogen more easy.

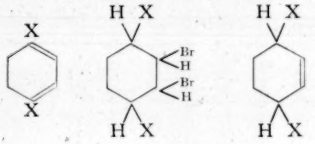
The $\Delta^{1.4}$ dihydro acid is formed by the action of boiling caustic soda on either of the acids already described. The structure of the acid follows from the reasoning already given, the action of caustic soda being to cause the double unions to shift *toward* the carboxyl groups. This acid was erroneously called $\Delta^{1.5}$ in Baeyer's first paper. The reasoning against Kekulè's formula based on the conversion of the dibromide obtained from this acid into terephthalic acid lost its force when the true structure was established. This acid is the most stable of all the dihydro acids, and either of the other dihydro acids is converted into it by boiling with caustic soda. The $\Delta^{1.3}$ acid is, however, less easily transformed in this way than any other.

The $\Delta^{1.3}$ dihydro-terephthalic acid is obtained by boiling the $\alpha\alpha'$ dibrom-hexahydro-terephthalic acid (obtained from the hexahydro

[1] Victor Meyer, Ber. d. chem. Ges. **20**, 534, 2944.

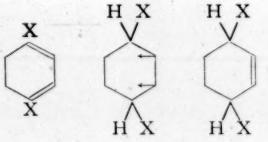
acid by direct substitution) with alcoholic potash. The proofs for the structure are:

1. The $\Delta^{1,4}$ dihydro acid takes up two molecules of hydrobromic acid and gives a *para*-dibrom-hexahydro acid which is converted into hexahydro-terephthalic acid by the action of zinc dust and acetic acid. The $\Delta^{1,3}$ acid, on the other hand, gives with hydrobromic acid an *ortho*-dibrom-hexahydro acid which gives the Δ^{2} tetrahydro acids when treated with zinc dust and acetic acid. The changes in the latter case are:



2. The dibromide of the Δ^{2} tetrahydro acid gives the same $\Delta^{1,3}$ acid as the *aá*-dibrom-hexahydro acid when treated with alcoholic potash.

3. Sodium amalgam reduces the $\Delta^{1,3}$ acid to the Δ^{2} tetrahydro acids, thus:



An analogy for this case was wanting, but was furnished by Baeyer and Rupe,[1] who reduced dichlor-muconic acid, $CO_2H.CH=CCl-CCl=CH-CO_2H$, and obtained the $\beta\gamma$-hydro-muconic acid, $CO_2H.CH_2-CH=CH-CH_2-CO_2H$. This last acid cannot be further reduced till the double union shifts to the $\alpha\beta$ position. It seems that in the reduction hydrogen atoms are added directly to the two carbon atoms combined with carboxyl groups, and that the valences of the other two carbon atoms then unite, forming a double union in the $\beta\gamma$ (or Δ^{2}) position. The $\Delta^{1,3}$ acid may also be reduced to the Δ^{2} tetrahydro acids by zinc dust and glacial acetic acid. This is the more remarkable as neither terephthalic acid nor any other of the hydro acids can be reduced in this way. This case shows very clearly the effect of the negative carboxyl groups in favoring the addition of hydrogen.

The $I^{\text{cistrans}}\Delta^{2}$ and the $I^{\text{vic}}\Delta^{2}$ tetrahydro-terephthalic acids are obtained by reducing the $\Delta^{1,3}$ dihydro acid with sodium amalgam or with zinc dust and glacial acetic acid; by reducing the $\Delta^{1,4}$ acid

[1] Ann. Chem. (Liebig) **251**, 278.

with sodium amalgam, and by reducing the 2.3 dibrom-hexahydro-terephthalic acid with zinc dust and glacial acetic acid. The structure follows from the methods of preparation, from the occurrence always of two "geometric" isomers, and from the fact that boiling with caustic soda converts both of the isomers into the Δ^1 tetrahydro acid. This is another instance of the shifting of the double union toward the carboxyl group under the influence of this reagent.

The Δ^1 tetrahydro-terephthalic acid is obtained by boiling the $\Delta^{1,4}$ dihydro acid, or terephthalic acid itself, with sodium amalgam, or by boiling the Δ^2 tetrahydro acid with caustic soda. The proofs for the structure are as follows:

1. The acid can have no *para* union between the carbon atoms, since it gives with hydrobromic acid a monobrom-hexahydro acid which is different from the α-monobrom-hexahydro acid obtained by direct substitution. The monobrom acid obtained from this acid must be a β-compound, and, since both the α and β monobrom-hexahydro acid give the same tetrahydro acid by treatment with alcoholic potash, the double union must be in the $\alpha\beta$ position.

2. The acid takes up two atoms of bromine, and the dibrom-hexahydro acid obtained is identical with the dibrom acid obtained from the β-monobrom-hexahydro acid by direct subs tution. When this dibrom acid is treated with zinc dust and glacial acetic acid, the tetrahydro acid is regenerated.

The I^{cis} and $I^{cistrans}$ hexahydro-terephthalic acids are formed by the reduction of the monobrom-hexahydro acids with zinc dust and glacial acetic acid. They are also formed by the reduction of any of the dibrom-hexahydro acids *which do not have the bromine atoms in the ortho position.* These acids conduct themselves in every respect as saturated compounds of the fatty acid series.

An interesting relation appears between the constitution of the acids and their solubility in water. A double union in the β position increases, while one in the α position decreases the solubility. A similar relation is also found for the melting points of the methyl esters.

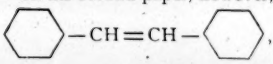
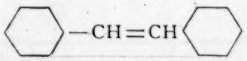
The most important result of the investigation is, perhaps, the proof furnished that terephthalic acid does not contain three para unions, and, hence, that the Claus formula as ordinarily understood cannot be true.

The partially reduced acids contain double unions between atoms in the ortho position. They have the character of true unsaturated compounds. They take up bromine and hydrobromic acid directly, and they all reduce permanganate immediately. This last property Baeyer[1] has shown to be a very valuable means for distinguishing between saturated and unsaturated com-

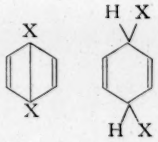
[1] Ann. Chem. (Liebig.) **245**, 146.

pounds. Terephthalic acid conducts itself in this respect as a saturated compound. Relying partly upon this and partly upon an erroneous structure for the $\Delta^{1,4}$ dihydro-terephthalic acid and the transformation of the dibrom addition product of that acid into terephthalic acid by alcoholic potash, Baeyer in his first paper drew the conclusion that Kekulè's formula cannot be true. He proposed in its place what he calls the "centric" formula, which he writes thus:

The idea which it is intended to express is that benzene contains a ring of six carbon atoms, and that one valence of each atom is directed toward the center of the ring. These valences mutually "paralyse" each other. They are held more firmly than is the case with double unions, since they are not attacked by permanganate, but less firmly than in the case of single unions, since terephthalic acid is reduced by sodium amalgam.

In his second paper, however, Baeyer says that while stilbene,  , reduces permanganate instantly, phenanthrene,  , does not. Whatever formula we assign to the two end benzene nuclei in phenanthrene the central nucleus must contain a double union. It seems, then, that this sort of a ring formation may give the double union the power to resist the action of permanganate and this objection to Kekulè's formula falls away.

In his final discussion, Baeyer seems to leave the question entirely open between the "centric" formula, Kekulè's and Dewar's. Dewar's formula seems to explain, most easily, the formation of the $\Delta^{2,5}$ dihydro acid by direct reduction, thus:



In view of the conduct of dichlor-muconic acid, however, Kekulè's formula also explains satisfactorily the formation of this acid.

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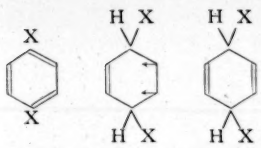
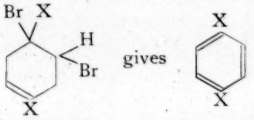


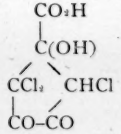
The transformation of the dibromide obtained from the $\Delta^{1,4}$ dihydro acid into terephthalic acid by alcoholic potash is explained most naturally by Kekulè's formula, thus:



Hantsch[1] has shown the formation of a collidin-dicarbonic ether from a dihydro compound containing the extra hydrogen atoms, one in combination with the nitrogen of the pyridine ring and the other in combination with the para carbon atom. This, perhaps, has a little weight in favor of Dewar's formula.

In the opinion of the author of this abstract, the lack of symmetry in Dewar's formula offers an objection very difficult to answer. It may be worthy of remark, also, that Dewar's formula ascribes to terephthalic acid two double unions in such a position as should render terephthalic acid easily soluble, while the position of the double unions in Kekulè's formula explains its difficult solubility.

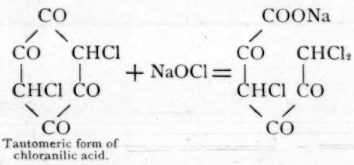
Hantsch has recently obtained some interesting results by the action of sodium hypochlorite on the chloranilic and bromanilic acids and on phenol. The first product obtained from chloranilic[2] acid was a trichlor-diketo-pentamethylene-oxycarbonic acid having the formula



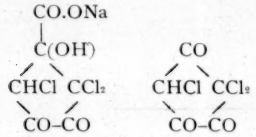
Under the influence of an oxidising agent this acid loses carbon dioxide and is converted into triketo-pentamethylene. This gives with phenyl-hydrazine a trihydrazone, which proves the presence of three carbonyl groups, and with bromine it gives trichlor-tribrom-acetone, $CCl_3Br.CO.CClBr_2$, and oxalic acid. The acid first

[1] Ber. d. chem. Ges. **18**, 2581. [2] Ibid. **21**, 2432.

obtained gives, also, an azine with toluylene-diamine, showing that it is an ortho-diketone. These reactions establish, conclusively, the formula which has been given. The transformations appear to take place as follows:

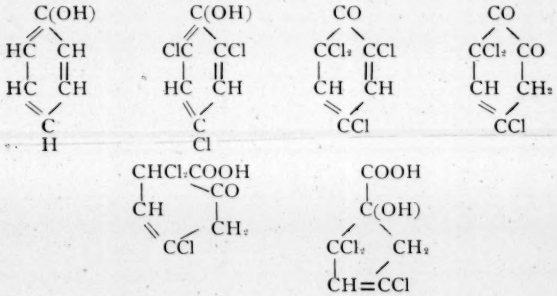


Tautomeric form of chloranilic acid.



Similar results were obtained with bromanilic acid.

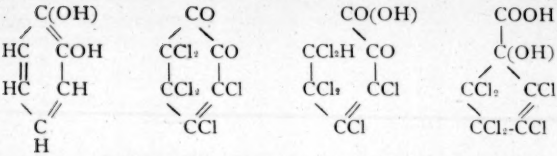
Chlorine acting upon a solution of phenol in caustic soda[1] also produces a compound containing a ring of five carbon atoms, thus:



The limits of this paper forbid a detailed discussion of these formulae.

Zincke[2] has found that similar compounds can be obtained from *o*-amidophenol and from pyrocatechin, thus:

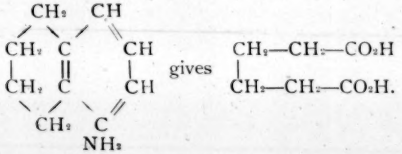
[1] Ber. d. chem. Ges. **20**, 2780; **22**, 1238. [2] Ibid. **21**, 2719, and **22**, 486.



From amido-β-naphthol and β-naphtho-quinone Zincke[1] has also obtained derivatives of indene and hydrindene in which one of the benzene rings of naphthalene has been transformed into a ring containing one less carbon atom.

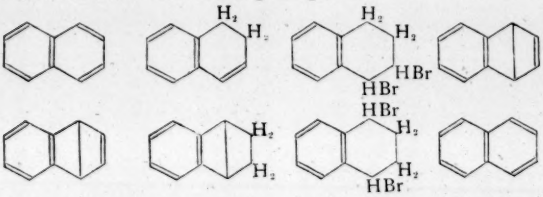
Nietzki and Benckiser[2] showed some time ago that croconic acid contains a ring of five carbon atoms, and that it can be formed from hexoxy-benzene.

Bamberger and Althouse[3] have obtained adipic acid by the oxidation of α-tetrahydro-naphthalene, thus:



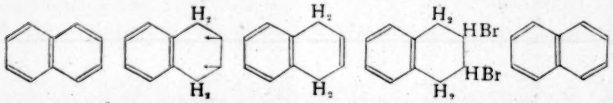
In this case a normal chain of six carbon atoms is obtained. This furnishes a very satisfactory proof that benzene contains a closed system of six carbon atoms, and also that hexamethylene is identical with hexahydro-benzene.

Bamberger and Lodter[4] have shown that dihydro-naphthalene gives a dibromide which is converted into naphthalene with the greatest ease. In a later discussion of this case, Bamberger[5] concludes that it is inconsistent with either Dewar's or Kekulè's formula for benzene, and gives the following scheme to show that if we accept either formula, the naphthalene obtained at the end must be different from that at the beginning.



[1] Ber. d. chem. Ges. **19**, 2493, etc., there are eleven or more papers on this subject.
[2] Ibid. **18**, 509, **19**, 308. [3] Ibid. **21**, 1895. [4] Ibid. **20**, 1706. [5] Ibid. **21**, 1903.

In view, however, of the reduction of the $\Delta^{1,3}$ dihydro-terephthalic acid to Δ^{3} tetrahydro-terephthalic acid, the following scheme seems justified.



This leads directly to Kekulè's formula.

In a discussion of the question of double union and of the formation of rings, Baeyer[1] some time ago proposed the following hypothesis as an addition to the Le Bel-Van't Hoff law: "The four valences of the carbon atom are exerted in the directions which join the center of a sphere with the corners of a tetrahedron inscribed within it and, hence, form an angle of 109° 28′ with each other. The direction of attraction can be turned from this normal direction, but a tension is produced in this way which increases as the angle through which the direction is turned increases."

Following this hypothesis, Baeyer shows that the interior angle of the regular pentagon (108°) varies but 1° 28′ from the normal angle for the valences of the carbon atom, while the interior angle of the hexagon is 10° 32′ greater than that of the normal angle. The ring of carbon atoms with five members should, by this reasoning, be the more stable.

If we consider Kekulè's formula in the light of this hypothesis, we find that the angle at each corner of the hexagon is that between the direction of one valence of a carbon atom and the plane of the directions of two other valences.[2] This angle is, normally, 125° 16′, and is only 5° 16′ greater than the interior angle of a hexagon. The tension produced in such a ring should, therefore, be considerably less than that of the hexa-methylene ring. If we consider the geometric forms represented by the formulae of Claus and Dewar and by the "centric" formula, it is evident that the configuration must produce a far greater tension than that of Kekulè's formula.

Not very much weight can be given to such speculations in the present state of our knowledge. The hypothesis seems to gain some support, however, from the marked tendency which has been discovered for benzene compounds to be transformed into compounds containing a ring of five carbon atoms. This tendency is, I believe, always associated with a transformation from the benzene toward the hexa-methylene type. W. A. Noyes.

[1] Ber. d. chem. Ges. **18**, 2278.

[2] Baeyer himself seems to interpret Kekulè's formula in a somewhat different way. Ann. Chem. (Liebig) **245**, 123.

Recent Researches on Cobalt and Nickel.

Since the publication, in January last, of the communication by Krüss and Schmidt[1] relative to the occurrence of a new metal in cobalt and nickel, several articles on this subject have appeared in the chemical journals. Krüss and Schmidt, in their investigation, made use of Clemens Winkler's method for the determination of the atomic weights of cobalt and nickel; Winkler therefore does not hesitate to express his opinion in regard to the reported discovery. His article[2] is, in substance, as follows: Having determined, after the appearance of the communication in question, to investigate again the action of cobalt and nickel on a neutral auric chloride solution, he prepares the chloride as follows: 1st, by heating gold in a current of chlorine; 2d, by action of chlorine gas on finely divided gold in water. A solution of the chloride prepared by the first method, when treated with a little sulphurous acid, assumes a deep cherry-red color. This is due to the formation of aurous sulphite, as subsequent analyses of the salt showed that it contained *aurous* chloride in proportion of 1 molecule AuCl to 23 molecules $AuCl_3$. To use such a substance for the determination of the atomic weight of cobalt and nickel (as Krüss and Schmidt have done) is, of course, inadmissible. On the other hand, the chloride prepared by the second method contains an excess of chlorine—one additional atom of chlorine to every three molecules $AuCl_3$ ($=Au_2Cl_{10}$). He prepares, also, sodium chlor-aurate (the substance used in his own determinations of atomic weights of cobalt and nickel), and the analyses of this show that it contains the gold exclusively in the form of trichloride. The action of cobalt and nickel, says Winkler, on a neutral sodium chlor-aurate solution is a simple one, and there are no secondary reactions. That Krüss and Schmidt should have reached a different conclusion must be due to the fact that they used impure cobalt and nickel. From their description of the action of the metals on the auric chloride solution, he thinks it very probable that the metals contained a small quantity of alkali. Non-reguline cobalt and nickel always show an alkaline reaction. Not only is this the case when the metals are obtained by reduction of their oxides, precipitated by alkalies, but even when obtained by reduction of their oxalates or chlorides, separated from acid solution. Even if the metals are converted into chlorides, and these are reduced anew by hydrogen, they will still show the alkaline reaction, and, strange though it may sound, it appears that even electrolytically precipitated cobalt and nickel may contain alkali. But though this alkali clings to the metals with such wonderful tenacity, investigations, even by spectrum analysis, have not shown with certainty what it is, or in what quantity it is present. If, now, such cobalt or nickel be introduced in a neutral auric

[1] Ber. d. chem. Gesell. 22, 11. [2] Ibid. 22, 890.

chloride solution, what Krüss and Schmidt observed actually takes place. An equivalent quantity of pure gold cannot be precipitated, and the gold always contains either cobalt or nickel, as the case may be. This is not caused by galvanic polarisation, as Krüss and Schmidt supposed, but only by the alkali contained in the cobalt or nickel. Winkler makes a number of similar investigations, always finds cobalt or nickel in the precipitated gold, but in no case is the presence of a third element detected. Cobalt and nickel free from alkali, and perfectly pure, precipitate from neutral auric chloride solution an equivalent quantity of gold free from cobalt or nickel. These metals can be prepared free from alkali and at the same time non-reguline, by sublimation of their pure chlorides in a current of chlorine, and subsequent reduction of the sublimate by hydrogen. It was material prepared in this manner that Winkler used in his atomic weight determinations.

An article by Dr. Fleitmann[1] is also of interest. The author, having been engaged in the nickel industry for many years, considered it his duty to endeavor to settle the question as to the existence of the new metal. He treats various samples of commercial nickel and cobalt oxides in the manner indicated by Krüss and Schmidt, and obtains negative results in every case. This, coupled with the fact that he had failed to receive a sample of the new metal promised him by Dr. Krüss, causes him to think it probable that the metal exists only in the imagination of its discoverers. Unwilling, however, to confront positive observations with negative results, he refrains from deciding the scientific side of the question, and awaits from Krüss and Schmidt the confirmation or revocation of their communication. In the meanwhile, in order to dispel the alarm occasioned amongst those engaged in the nickel industry, he expresses, in the following terms, his convictions, founded on personal investigations: First: if a new metal really exists, as a regular companion of nickel and cobalt, it is present in extremely small quantities, nothing like 2 per cent. Secondly, such small quantities will have no essential influence on the ductility of nickel, which, in its present purity, is as malleable and ductile as the softest iron. Thirdly, the methods, patented by Krüss for the purification of nickel, are without practical value, as they are in part not new, in part not practical. If, says Dr. Fleitmann, commercial nickel or cobalt, in the form of hydroxide, is treated with large quantities of sodium hydroxide, in the manner described by Krüss and Schmidt, various impurities, such as alumina, lead, zinc and cerium oxides, arsenic, manganic, molybdic, silicic and chromic acids, etc., are dissolved, and, in connection with these, a small quantity (usually not more than $\frac{1}{10}$ per cent. of the oxide used) of nickelous and cobaltous oxides. If the nickelous and cobaltous oxides are separated from the other impurities dissolved in the alkaline extract, they are now found to

[1] Chemiker Zeitung **13**, 757.

be insoluble in sodium hydroxide. Hence it appears that their original solubility was occasioned by the presence of those impurities, especially by arsenic acid, silicic acid and alumina. If to the alkaline extract above mentioned, hydrochloric acid be added, until the precipitate that forms is redissolved, and then ammonium carbonate, a wondrous mixture of different oxides and acids is obtained. The author thinks it probable that it was with such a mixture as this that Krüss and Schmidt had to deal.

The investigation of Krüss and Schmidt is far from complete as yet, but they have very recently made a short communication[1] relative to its progress. Having obtained, after the most careful purification, a specimen of nickel in which no known impurity can be detected, they endeavor to ascertain the equivalents of the two oxides into which nickel oxide can be separated. This separation is effected by methods previously described by them, as well as by fractional precipitation of basic nickel-ammonium arsenite. Determinations of the atomic weights result as follows: For the metal of lower atomic weight 56 to 58. For the metal of higher atomic weight 61 to 100. Hence the atomic weight of the former appears to be somewhat lower than the atomic weight of nickel, as at present accepted, and that of the latter considerably higher. After these determinations the metals are subjected again to an exact qualitative investigation, which convinces the authors that they contain no known impurities which, in the one case, would tend to lower the atomic weight of nickel, or, in the other, would tend to raise it. These results confirm their former supposition as to the compound nature of nickel; still it is at present doubtful whether it is a mixture of two or of several metals, and hence they refrain from a discussion of the relation of the atomic weights of the two portions to the periodic system. Consideration of Mr. Winkler's article is reserved for a later and more extended communication.

C. C. BLACKSHEAR.

A TREATISE ON THE PRINCIPLES OF CHEMISTRY. By M. M. Pattison Muir, M. A., F. R. S. E., Fellow, and Prælector in Chemistry, of Gonville and Caius College, Cambridge. Second Edition. Cambridge: University Press. 1889. 490 pp. 8vo.

In the first edition of this book Mr. Muir made an earnest effort to treat the general principles of chemistry in a scientific way, and in many respects he was markedly successful. The book, however, lacked clearness. It was by no means an easy matter always to tell what object the author had in view, and the relations between the different parts could not be clearly recognised. It is evident that the author himself was conscious of this defect, and he has attempted to remedy it. In the preface to the second edition he

[1] Ber. d. chem. Ges. 22, 2026.

says: "The aim and scope of the book have not been changed. The whole has been thoroughly revised, and Book II has been entirely rewritten. The revision will, I hope, make clearer than before the mutual dependence of the parts.

"Since the first edition was published, much important work has been done on subjects treated in Book I; the results of this work have been noticed in the present edition; at the same time some chapters have been shortened, especially that dealing with valency and isomerism; the arrangement of these, and some other chapters has been altered. The chapters on physical methods have been rewritten.

"When the first edition was published, the study of chemical affinity was entering on a new phase; since 1884 progress has been very rapid, and to-day we are much nearer the goal than we were five years ago. The great importance of recent work on affinity has compelled me entirely to rewrite Book II. In doing this I have largely followed Ostwald's *Lehrbuch der allgemeinen Chemie;* without that admirable treatise, the part of my book dealing with affinity could not have been written. I am anxious to express, as strongly and warmly as I can, my indebtedness to Prof. Ostwald."

A careful examination of the new edition shows that the revision does in fact "make clearer than before the mutual dependence of the parts." The book is in every way an improvement upon the first edition, and it will no doubt find a larger field of usefulness.

The author's attempt to frame an unassailable definition of valence leads him to the following: "*The valency of an atom is a number which expresses the maximum number of other atoms between which and the specified atom there is direct interaction in any gaseous molecule.*" This definition would seem to be too narrow. It is certainly simpler to restrict the conception to gaseous molecules, and the results are more trustworthy, but surely there are cases in which the study of composition, taken together with that of chemical transformations, can lead to conclusions of value with regard to the subject of valence. If it is found that by making a simple assumption a large number of otherwise wholly incomprehensible chemical reactions can be explained, it is just as well for the time being to make the assumption, and then see what comes of it. But we must of course not forget that we have made the assumption. There is great danger that we shall forget it, but that is true of every working hypothesis, and yet we cannot do without them. It would simplify chemistry very much indeed if all compounds and all elements could, without decomposition, be converted into perfect gases. We have to take things as they are. In spite of objections which can be raised, however, Mr. Muir's caution is wholesome, and the lesson he is teaching is loudly called for. In regard to the objection above mentioned, the author says (p. 243): "But it may be urged that a much wider meaning ought

to be given to the term valency. Better, I would reply, employ another term or other terms. Let us make as much use of valency as we can; so far as it goes it is definite, without it the chemistry of carbon compounds especially could not have made the advances which it has made. But it is not all." It is difficult to see how the introduction of another term or other terms would help the matter. Before we can hope to gain a satisfactory knowledge of valence it is necessary that we should group together the phenomena of valence. Now it would seem that the introduction of new terms for the purpose of designating some of these phenomena would hinder rather than further progress.

It should be said that the point which is here criticised is of minor importance as far as the book is concerned. There is, further, room for an honest difference of opinion, and it is well for chemists that the subject of valence should be presented to them from the author's point of view. Radical treatment is necessary in many cases.

Book II which, as the author distinctly tells us, is based upon Ostwald's *Lehrbuch der allgemeinen Chemie*, is clearly written and will be of great service to students. Whatever may have been the case a few years ago, it is certainly true now that no chemist can afford to be without a knowledge of the recent developments in the study of affinity. These developments are unquestionably among the most important that chemistry has to show of late. The most recent results have been incorporated in the book, and it can be cordially recommended to students.

I. R.

WATTS' DICTIONARY OF CHEMISTRY. Revised and entirely rewritten by H. FOSTER MORLEY, M. A., D. Sc., and M. M. PATTISON MUIR, M. A., assisted by eminent contributors. In four volumes. London and New York: Longman, Green & Co., 1888, 1889. Price $14.50 a volume.

The first edition of this work was published twenty-five years ago. It appears from the preface of the new edition that "some time before his death Mr. Watts had agreed to prepare a new edition of his dictionary, which should give as complete an account of the present state of the science as might be found compatible with the appearance of the book in four volumes of 750 pages each." After the death of Mr. Watts the work planned and begun by him was taken up by the present editors, and two volumes of the dictionary have already been published. In order to keep within the prescribed limit of four volumes a very condensed style has been adopted, abbreviations are freely used, and formulae are frequently employed instead of names. Further, the new edition treats of chemistry only, whereas the old edition had to deal also with "the allied branches of other sciences." No special information is given with regard to chemical technology,

though "technical chemistry will be treated in a companion volume to be published under the editorship of Professor Thorpe." Details in regard to analytical processes have, in general, been omitted. The free use of abbreviations throughout gives the pages a confused appearance, but it requires only a little practice to enable one to read the matter readily. Although the number of organic compounds has doubled since the appearance of the first edition, "nevertheless the space allotted to them in the present dictionary is little more than quarter of that devoted to organic chemistry in the original dictionary and its supplements." Besides the articles on special subjects, there are many on general subjects. Among those in the first volume which are worthy of special note are the following: Allotropy, by Lothar Meyer; Affinity, by W. Ostwald; Acids and Alloys, by W. Ramsay; States of Aggregation, by J. J. Thomson; Bacteria, by E. Ray Lankester; Chemical Change, by J. J. Hood; Azo-coloring Matters, by Raphael Meldola; Atmosphere, by T. E. Thorpe; Ash of Organic Bodies, by R. Warington; and Atomic and Molecular Weights, by Mr. Muir. In the second volume the following are of special importance: Chemical Equilibrium, by J. J. Thomson; Dissociation and Explosion, by R. Threlfall; Elements, by F. W. Clarke; Combustion and Flame, by T. E. Thorpe; Crystallisation, by Harry Baker; and Laws of Chemical Combination, by Mr. Muir.

The names of the editors and of the special contributors give us confidence in the accuracy and thoroughness of the book, a confidence which is strengthened by an examination of a number of the articles. It appears that in the new Watts' Dictionary chemists have an extremely valuable, compact work of reference which must become a necessity in every well-stocked chemical library.

I. R.

A Text-Book of Organic Chemistry. By A. Bernthsen, Ph. D. Translated by George McGowan, Ph. D. London: Blackie & Son, 1889; and New York: D. Van Nostrand Company, 1889.

The original book, of which this is a translation, is considerably smaller than Richter's well known treatise on the same subject, and is intended for those who are in the early stage of their study of organic chemistry. It is clearly written, and must be helpful to students who have already acquired some knowledge of the compounds of carbon. For the beginner it contains too much, as is the case with nearly all so-called elementary treatises on the subject. Its use should be preceded by that of some still smaller book, in which stress is laid upon the system rather than on the properties of individual compounds. With some knowledge of this system, the student can then proceed with advantage to a more thorough study of the subject as it is presented in this book.

The translation is not entirely satisfactory, though it is better than most translations of German books on chemistry. The following curious passage occurs on p. 15: "With the setting up of the type CH_4 by Kekulé, and the knowledge of the tetravalent nature of carbon accompanying this, were connected the endeavors of Kolbe to derive the constitution of organic compounds from carbonic acid, but from an incomplete grasp of the subject of equivalent proportions a clear insight into this was not arrived at." It is a little difficult to see exactly what is meant by this, but one thing is clear, and that is that Mr. Bernthsen thinks Kolbe had "an incomplete grasp of the subject of equivalent proportions." The student who may use the book is advised to read the original papers on the subject referred to, before coming to the conclusion that Kolbe had an incomplete grasp of it.

I. R.

A Manual of Assaying Gold, Silver, Copper and Lead Ores. By Walter Lee Brown, B. Sc. Third Edition. Chicago: E. H. Sargent & Co., 1889.

This book, to quote from the preface, "is written as a guide to those who having had no previous technical or especially scientific education, desire to learn something of the practical assaying of gold and silver ores." It is an excellent book; clear and concise, it covers all the practical difficulties which the beginner meets. It can be especially recommended to chemists, who will find that backed by their knowledge of the chemical changes involved in assaying, they need no further help to become good assayers with practice.

E. R.

NOTES.

On the Separation of Copper from Cadmium.

The two methods which are in use at present for the separation of these two substances, while they are both good and efficient in the hands of experienced persons, nevertheless present some difficulties when placed in the hands of the beginner. The best one, and the one generally given in most books on qualitative analysis, depending on the difference in conduct of the double cyanides of copper and cadmium towards hydrogen sulphide, is objectionable, for the reason that it involves the use of potassium cyanide, a substance the use of which by the average young student had

better be avoided unless he is under the constant supervision of the instructor. My own experience as a teacher has shown me also that in the hands of those just beginning the study of qualitative analysis, the other method, depending on the difference in the solubility of the sulphides of these two metals in dilute sulphuric acid, is far from yielding satisfactory results.

The following simple method involves the use of no reagent which would be likely to prove harmful, and it has given good results even in the hands of very unskilled persons. The method depends upon the fact that metallic iron precipitates the copper completely from solutions containing copper and cadmium and leaves the cadmium in solution.

The method of procedure is as follows: The filtrate from the bismuth, if seen to contain copper either by its blue color or by giving the characteristic red color with potassium ferrocyanide in the presence of acetic acid, is acidified with dilute nitric acid and evaporated to dryness, and the residue heated until the nitrates are decomposed. The mass is then treated with a few drops of concentrated hydrochloric acid, and the solution diluted with about five times its bulk of water and filtered into a test tube. Metallic iron (fine piano wire is a good form to use) is now added to this filtrate, and the tube and its contents are then heated in a water-bath until the solution is perfectly colorless. The temperature of the bath need not exceed 80° C., and the solution containing the chlorides of copper and cadmium should be acid enough to cause a slow evolution of hydrogen at this temperature. Under these conditions the copper is rapidly precipitated on the iron, and I have generally found that an hour's heating on the water-bath is sufficient to precipitate all of the copper, even when present in comparatively large quantity. When the precipitation of the copper is complete, the colorless solution is filtered from the copper and the excess of iron, diluted with an equal quantity of water and treated with hydrogen sulphide. A yellow precipitate indicates cadmium. The copper can be easily recognised by the red color of the precipitate on the iron, but, of course, the presence or absence of this substance must be inferred from the color of the filtrate from the bismuth.

The satisfactory results obtained by this method lead me to believe that instructors will find it to their advantage to use it with students who who have had but little experience in laboratory work.

J. H. KASTLE.

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Decomposition of Potassium Chlorate by Heat in the presence of Manganese Dioxide.

In view of the obscurity of the knowledge in regard to the cause of the ready decomposition of potassium chlorate when heated in

the presence of manganese peroxide, an investigation of the subject was undertaken by Herbert McLeod.[1]

The experiments were conducted in a very simple manner. The mixture of potassium perchlorate and manganese peroxide was placed in a small test tube connected with a U tube containing a solution of potassium iodide. The test tube was then placed in a larger test tube containing mercury, and this was heated until the vapor of the mercury rose above the mixture in the small tube, corresponding to a temperature of about 358° C. The oxygen liberated was determined by difference in weight before and after the operation, less the weight of chlorine evolved. This last displaced the iodine in the solution of potassium iodide, and its amount was determined by titration with sodium thiosulphate. Various kinds of oxides of manganese were used in the experiments; and several of the experiments were viewed through a microscope.

As a result of these experiments, McLeod concludes that the reaction takes place as follows: In the first place, the potassium perchlorate and manganese peroxide react upon each other, forming potassium permanganate, and liberating chlorine and oxygen, thus

$$(1) \qquad 2KClO_3 + MnO_2 = K_2Mn_2O_8 + Cl_2 + O_2.$$

Under the influence of heat the permanganate is then decomposed into potassium manganate, manganese peroxide and oxygen, thus:

$$(2) \qquad K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2.$$

Finally the manganate so formed is attacked by the chlorine, giving potassium chloride, manganese peroxide, and oxygen.

These conclusions are based upon the following observations: in regard to (1), he found that chlorine is undoubtedly given off in the early stages of the reaction, and that if some substance which will take up chlorine, for example sodium carbonate, be added to the mixture, the decomposition is incomplete. After this action permanganate was found in the mass. He also noticed that if a small quantity of peroxide be used, the fused mass is pink, and if this is now heated in mercury vapor, the color remains until all the potassium chlorate is decomposed, then turns green and finally brown. Now if this pink color is due to permanganate, then the latter is being continually formed, because if potassium chlorate and potassium permanganate are heated together, the permanganate is decomposed between 250° and 275° C. The fact that the permanganate decomposes at this temperature is proof of the second stage of the reaction (2).

The evidence in favor of (3) is based upon the fact that when the reaction is complete a black powder is found sticking to the sides of the tube. This is probably regenerated manganese peroxide. Moreover, when chlorine is passed into the mass resulting from the fusion of potassium permanganate, the chlorine is

[1] J. Chem. Soc., April, 1889.

absorbed and oxygen is given off. At ordinary temperatures both potassium chloride and manganous chloride would be formed, but at the temperature of mercury vapor manganous chloride is decomposed, yielding an oxide of manganese and chlorine.

In addition to these facts, McLeod shows that with very small quantities of manganese peroxide the action is complete, but takes place much more slowly, and that the same peroxide can be used repeatedly for a similar purpose, but it changes in appearance from brown to black, showing that it has taken part in the chemical action and has been reproduced. A bright crystal of pyrolusite used in one experiment was changed to needle-shaped fragments. An interesting experiment was made to determine whether the peroxide served only for supplying nuclei for gas evolution. To this end platinum black, a chemically inert substance, was substituted for the peroxide and the experiment conducted as before. The reaction took place to a limited extent only. He concludes from several observations made with the microscope, that only a portion of the manganese peroxide is changed, the rest acting as nuclei for gas evolution.

CHAS. H. HERTY.

Some Modifications of the Kjeldahl Method for Estimating Nitrogen.

Several modifications of the Kjeldahl method for estimating nitrogen have recently been published. F. Martinotti[1] finds that, in case no nitrates are present in the substance to be analysed, the original method of Kjeldahl gives results which agree amongst themselves and compare very favorably with the results obtained by the method of Dumas.

In case nitrates are present, however, neither the original Kjeldahl method nor Jodlbauer's modification (*i. e.* where phenolsulphonic acid is used) gave good results. The percentage of nitrogen was always found to be too low, and varied with the length of time during which the heating was continued. It was found best to estimate the nitrogen which was in the form of nitrates by Schlösing's method (*i.e.* by the use of ferrous chloride and hydrochloric acid). The nitrogen in other forms than nitrates is best estimated as follows: The weighed substance is treated with ferrous chloride and hydrochloric acid and evaporated to dryness, thereby eliminating the nitrates. The nitrogen in the residue is then estimated by the plain Kjeldahl method.

O. Foerster[2] also finds that neither the original Kjeldahl method nor the modification in which phenolsulphonic acid is used gives accurate results. All of the nitrogen of nitrates is not converted into ammonia, and the results, consequently, are too low. He finds that sodium thiosulphate converts nitric acid into nitrosyl-sulphuric acid, thus:

[1] Ztschr. anal. Chem. **28**, 415. [2] Ibid. **28**, 422.

$$4HNO_3 + 4H_2SO_4 + Na_2S_2O_3 = 4SO_3{<}^{NO_2}_{HO} + 2NaHSO_4 + 3H_2O,$$

and nitrosyl-sulphuric acid is readily converted into ammonia. He therefore recommends that sodium thiosulphate be added to the contents of the digestion flask after the action of the phenol-sulphonic acid has continued for some time. In this way good results are obtained.[1]

J. W. Gunning[2] finds that the addition of potassium sulphate to the sulphuric acid which is used in the plain Kjeldahl method greatly facilitates the complete oxidation of the organic matter. In the unmodified method the sulphuric acid gets so weak towards the end of the operation, from the loss of sulphur dioxide and from dilution by the water formed in the reaction, that the oxidation proceeds very slowly. By the addition of potassium sulphate to the sulphuric acid, potassium acid sulphate is formed, and this gives up water rather than sulphuric acid. In the process of heating, therefore, the water is constantly distilled off, and the acid, instead of getting weaker, gets stronger. By this method the complete oxidation of the substance, until the contents of the flask are perfectly colorless, is generally effected in from ½ to 1 hour, and never takes more than 2 hours with the most difficultly oxidisable substances.

R. DE ROODE.

A Simplified Fat-Extracting Apparatus.

The Soxhlet extracting tube, notwithstanding its effectiveness, is nevertheless open to objections on account of its complicated construction and consequent expense. When one of the small tubes is broken the whole instrument is rendered useless.

Recently, while conducting some analyses under Mr. Walter Maxwell in the Harvard Chemical Laboratory, it occurred to me that this apparatus could be simplified without detracting from its effectiveness. The apparatus which I devised consists of three pieces:

1. A piece of glass tubing 4 cm. wide and 20 cm. long is drawn out at one end so as to pass through a rather large hole in a cork.

2. A large-sized test-tube is fitted into the larger tube so as to come within 3 cm. of the top.

3. A glass tube of small bore, best about ½ cm. bore, is bent in such a way that one end reaches to the bottom of the inner test-tube, while the other goes between the inner and the outer tubes and reaches into the part of the outside tube that has been drawn out. This end can be slightly bent so as to accommodate itself to

[1] *Note by Abstracter.*—No mention is made either by Martinotti or Foerster of the modification of M. A. Scovell, of the Kentucky Agricultural Experiment Station (*i. e.* where salicylic acid is used in the place of phenol), which, in the case of potassium nitrate, gives remarkably accurate results.

[2] Ztschr. anal. Chem. **28**, 188.

the outside tube. To set the apparatus up, hang the bent tube over the top of the larger of the two large tubes, and place these in the piece first described. The bottom of the latter is connected with a small flask, while the upper portion is connected with a condenser. The substance under examination is placed in the inner tube after having been wrapped in a piece of filter paper. As soon as the distillation begins, the ether or alcohol passes from the flask through the outside tube, is condensed, and falls into the inner tube. Just before the inner tube has become filled, the capillary attraction draws the liquid through the siphon, and the whole liquid contents with the extracted fats are siphoned into the flask below.

At first I had some difficulty in getting the apparatus to work satisfactorily because of the inner tube settling down below the top of the siphon, but with a little care this difficulty can be avoided. I have used several of these extractors with satisfactory results. The apparatus is very easily constructed out of ordinary glass tubing. It certainly has two characteristics to recommend it, viz. simplicity and neatness.

J. T. CRAWLEY.

International Congress of Chemists.

An International Congress of Chemists was held in Paris during the past summer. Many questions of interest were discussed, and it was finally decided to appoint an International Commission to consider the subject of chemical nomenclature. The commission consists of: Messrs. Berthelot, Friedel, Béhal, Bouveault, Gautier, Schützenberger, Grimaux, Jungfleisch, Fauconnier, Combes (France); Graebe (Switzerland); Alexeieff, Beilstein (Russia); Baeyer, Nölting (Germany); Lieben (Austria-Hungary); Franchimont (Holland); Paterno (Italy); Armstrong (England); Istrati (Roumania); Ira Remsen (United States); Calderon (Spain); Bonkowski-Bey (Turkey); Cléve (Sweden); Mourgues (Chili). An abstract of the proceedings of the meeting of the Congress will be given in a later number of this Journal.